Synthesis of Aqueous Polymer Colloids Based on Saccharide Monomers and Alkyl Acrylates Through Emulsion Polymerization

Von der Gemeinsamen Naturwissenschaftlichen Fakultät
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Congress contributions (Posters)

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2. Mohamed AL-Bagoury, Barbora Vymetalikova, Emile-Joseph Yaacoub; "Sugar Latexes as a New Type of Binder for Water-Based Paint and Coating", XXVI FATIPEC Congress "European Organization of Paint Scientists and Engineers", 9-11 September (Dresden) 2002,137

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TO MARYAM, YASMEN AND ABIR

LIST OF CONTENT

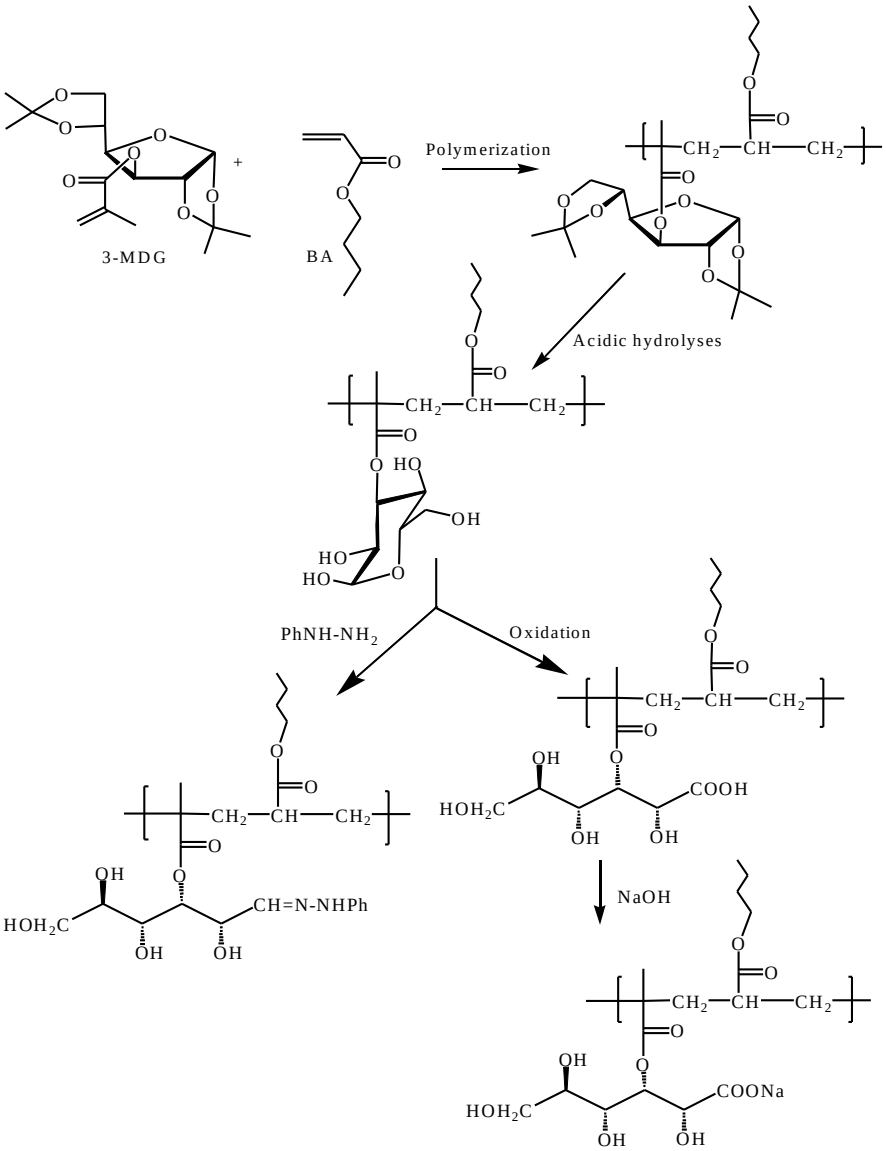
INTRODUCTION

The subject of renewable resources (RR) has attracted great interest in the last 30 years. The annual production of biomass is about 170 billion tons (170 x 10^9 tons). In comparison, the total reserve of mineral oil worldwide is about 135 billion tons. From the total amount of the biomass, only about 6 million tons (3.5%) are used by humans. From this 6 million tons biomass, less than 8% goes to the chemical industry. The entire raw materials use of the German chemical industry amounted in 1991 was 22.4 million tons: 18.4 million tons oil (82%), 1.7 million tons of natural gas (8%), 1.8 million tons renewable raw materials or RR (8%) and 0.5 million tons of coal (2%). The 1.8 million tons of RR divided themselves as follows: 900.000 tons of fats and oils (50%), 465.000 tons of starch (28%), 250.000 tons of cellulose (14%), 32.000 tons of sugars (2%) and 100.000 tons other natural substances. These numbers show that a large or complete substitution of fossil raw materials by RR is not possible. Some restrictions, which faced the use of RR in the chemical industry, were reasoned as follows: i) presently available crops are mainly designed and grown for nutritional purposes and not for industrial use; ii) the low prices of the petrochemical products inhibit the market of the renewable resources. Nevertheless, regenerating raw materials are competitive in many ranges in relation to synthetic products. In addition, it requires, however, the intelligent use of its special functional characteristics such as the biocompatibility and the possible biodegradability, which play special role in the balancing of CO_2-balance. It is particularly attractive in the utilization of these materials, if the synthetic achievements of nature can be used partially or to a large extent to reach the desired product and its specific quality.

Indeed, there are cooperation's established between many professional groups such as farmers, agronomists, botanists, ecologists, chemists, economists, politicians, and others in order to find a new perspective for the utilization of renewable resources as chemical feedstock. It is predicted that till 2090 about 90% of organic chemicals in USA will base on renewable resources. In the future, some factors could increase the markets of renewable resources such as an increase in price of the crude oil, and/or a decrease in price of RR, more basic and applied research for RR, increasing of the importance of ecological advantages of RR based products. The utilization of low molecular weight carbohydrates as renewable resources for the preparation of monomers and their corresponding polymers is one of many applications for RR.

From this point of view we present this work, which we consider it as a small step towards a great development in the field of renewable resources. The synthesis of new polymer materials in form of polymer particles dispersed in water (latexes) based on renewable resources, such as

glucose derivatives, has attracted our interest. Saccharide based latexes prepared through emulsion polymerization are promising with many possibilities of application in different fields like paints, coating, adhesives, medicine, pharmacy, cosmetic and analytics.



Scheme 1. Copolymerization of 3-MDG/BA and the subsequently chemical modification of the copolymer.

The free radical emulsion polymerization of saccharide monomers combines two main advantages: the first is the use of monomer based on saccharide derivatives to obtain tailor-made polymers with high functionality, biocompatibility, possibly biodegradability, low toxicity, optical activity, good thermal and mechanical properties, etc. The second main advantage is the use of an environmentally friendly process such as the emulsion polymerization, the widely used industrial polymerization process. This technique presents many advantages compared to other polymerization processes such as the use of water as reaction medium, high solid ratio, low viscosity, high productivity, and synthesis of high molecular-weight polymers, etc.

The aim of this work was directed to study the emulsion copolymerization of a methacrylate monomer containing glucose moiety by means of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG) with alkyl (meth)acrylates such as butyl acrylate (BA) (scheme 1). The synthesis of 3-MDG in a two simple steps reaction with high yield could improve the chance for an industrial scale up. 3-MDG as a hydrophobic monomer with very low water solubility, about 0.2% at 60 °C, is a good candidate for emulsion polymerization. The homopolymer of 3-MDG exhibits good thermal properties and has a high glass transition temperature (T_g) value of 167 °C. Due to the rigid structure of the saccharide ring, it is considered as a hard component. BA was chosen as soft component (T_g= -54°C) to optimize the desired thermal and mechanical properties of the copolymers. The free radical emulsion copolymerization of this binary system 3-MDG/BA was carried out with different polymerization processes.

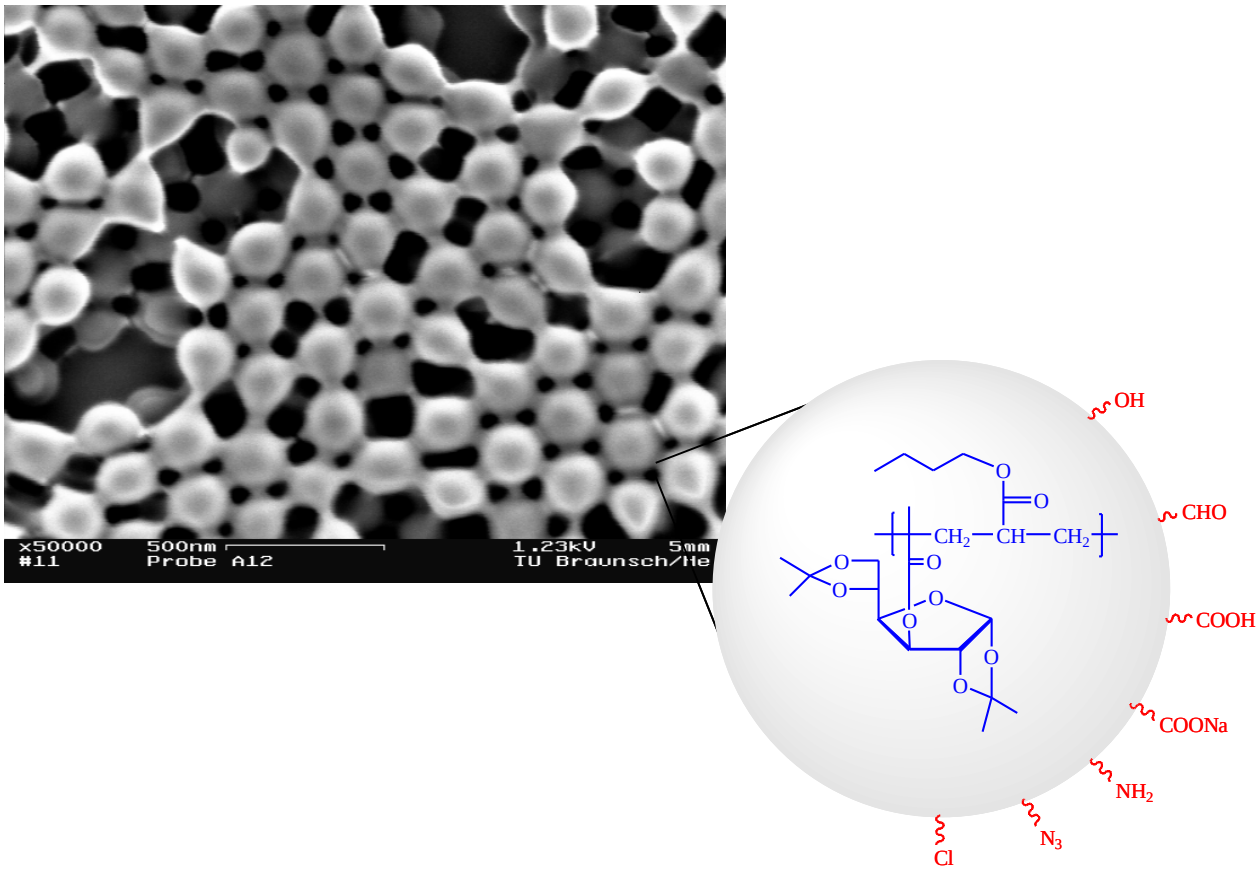


Figure 1: Chemical structure of the modified and functionalized end latexes.

The formed latex can be used as it or can be further modified. For example the protecting groups of the saccharide derivative could be removed by hydrolysis, to yield a polymer containing hydrophilic glucose units with one primary and three secondary hydroxyl groups, or through tautomerization an aldehyde group (linear structure). The later can undergo further chemical

modifications such as oxidation or reduction reactions. These modifications for further specific applications can be conducted either directly on the polymer colloid or on the pure precipitated copolymer. Scheme 1 represents the chemical structure of 3-MDG/BA copolymer and shows some examples of the possible chemical modifications. Figure1 shows monodisperse sugar latex and the possible chemical functionalization of it.

This work is broken down into five chapters as follows:

- The first chapter sheds the light on four points: preparation of monomers containing mono- and disaccharides moieties, emulsion polymerization and the semicontinuous process, miniemulsion polymerization, and living radical polymerization by means of reversible addition fragmentation chain transfer (RAFT) in dispersed media.
- The second chapter describes the semicontinuous emulsion copolymerization of 3-MDG and BA by using the monomer-feed addition technique. Some reaction parameters were varied to produce a water dispersed polymer with wide variety of properties.
- The third chapter deals with the semicontinuous emulsion copolymerization of 3-MDG and BA by the pre-emulsion technique. The studies included the effects of the polymerization variables (emulsifier, initiator, buffer, addition strategy) on the colloidal (particle size and particle size distribution), thermal (glass transition temperature), mechanical (film formation and tensile strength), and rheological properties.
- The fourth chapter represents, for the first time, the miniemulsion technique to prepare latex containing saccharide moieties via free radical polymerization. The behavior of the hydrophobic glucose methacrylate monomer in miniemulsion polymerization and the type of nucleation mechanism, monomer droplets or other mechanism, were studied. Also, some important reaction parameters such as the emulsifier type, its concentration, initiator type and its concentration were investigated.
- The last chapter presents the living radical polymerization in miniemulsion as a new technique to synthesize polymers with a desired microstructure and narrow molecular weight distribution. Three RAFT agents based on dithiobenzoate derivatives, with different activity towards 3-MDG, were investigated. Furthermore, block copolymers based on saccharide carrying polymers with some alkyl (meth)acrylates were synthesized. The deprotection of the formed block copolymer, poly(3-MDG-*b*-BMA), by means of acid hydrolysis yields an amphiphilic block copolymer. The properties of this polymer which depend on the length of each block were studied.

The laboratory investigations in this work could be considered as a good basis for possible scale up of this system on an industrial level.

Chapter 1

Theoretical Basis

Symposia:

In this chapter, an overview will be given on the following points; i) the synthesis and polymerization of saccharide based monomers, ii) emulsion polymerization and the semicontinuous processes, iii) miniemulsion polymerization, and iv) living radical polymerization in dispersed media and the mechanism of reversible addition fragmentation chain transfer (RAFT) technique.

1.1. Low molecular weight carbohydrates as monomers

Carbohydrates are the most abundant group of natural products. Every year 127 billion tons of carbohydrates are produced by photosynthesis in plants and microorganisms. The pioneer work from Emil Fischer at the beginning of the 20th century has put the basics of the carbohydrate chemistry and opened the door to a great development in this field. In the early of 20th century, many attempts were undertaken to utilize the carbohydrates as raw materials for the chemical industry especially for polymer production. In spite of all the difficulties in this way, researchers from many fields are doing the best efforts to reach this goal.

Nowadays, millions of tons low molecular-weight carbohydrates such as D-glucose, D-fructose, sucrose, lactose, maltose and others are industrially available with high purity and that enhances the activities for the chemical utilization of such materials in non-food applications. Furthermore, their intrinsic highly hydrophilic character as well as their low irritation and compatibility with skin and other biological surfaces led to increase the interest for their use in the domain of polymer synthesis to prepare biocompatible materials with favorable pharmacological and cosmetic properties. The durability/stability of these materials is also an important factor for possible industrial use. Numerous examples of synthetic polymers containing carbohydrate residues such as D-glucose, L-sorbose, D-xylose, D-galactose, D-mannose, 1-amino-1-desoxy-D-glucitol, sucrose, cellobiose, and others have been reported in the literature.

A brief review on the synthesis and polymerization of some saccharide based monomers will be given here. It is difficult to cover all the published works in this field, nevertheless only an idea about different types of monomers and different polymerization techniques will be presented. It is worthy to note that there are many monographs, which were published in this field in the last 20 years [1-10].

The presence of many hydroxyl groups with relatively different activities and also other reactive groups, such as carbonyl and amino groups, in the saccharide moieties makes the introduction of a polymerizable double bond to saccharide moieties to prepare a saccharide monomer a difficult task. The early attempts at the beginning of the 20th century to prepare allyl carbohydrates such as α- and β-allyl glucosides, 3-allyl glucose and α- and β-allyl galactosides have been reported [11]. Also, allyl ether of α-methyl glucose and sucrose were described [12]. The preparation of tetra-allyl α-methyl glucoside and its polymerization in 1944 was published. Under the influence of oxygen and heat, the allyl-glucoside gradually polymerized, first to a viscous liquid and finally to a colorless transparent thermosetting resin. Allyl sucrose was also prepared in a 68%

yield based on 7 allyl groups per sucrose molecule. In 1945, Yanovsky et al. [13] reported on the preparation of glucose pentamethacrylate (GPM) by direct addition of methacrylic anhydride to D-glucose at 65 °C for 3.5 h. GPM monomer was soluble in most organic solvents. The free radical polymerization of GPM was carried out in chloroform and other solvents for 2 h at 100°C using benzoyl peroxide or cobalt naphthenate as initiator. GPM polymerized slowly in the presence of benzoyl peroxide at room temperature in more than one month. Maltose octamethacrylate was prepared by addition methacrylic anhydride to maltose. A solution of maltose octamethacrylate in chloroform (50%) was gelled in 15 days at room temperature indicating the end of polymerization.

From the previous examples we can confirm that it was impossible to synthesize specific saccharide monomers with selective addition of one polymerizable group to the saccharide moieties. Only, it was possible to prepare monosubstituted monomers by direct attachment of the double bond at the anomeric center (C-1 of glucose for example).

With the development in the chemistry and technology of carbohydrates and the characterization methods, it is being easier to synthesize tailored monomers with a designed structure. The introduction of protecting groups is widely used in the chemistry of carbohydrates. Various strategies are used to protect selectively one or more hydroxyl groups of the saccharide unit and then to introduce the polymerizable group through etherification or esterification reactions in the desired position of the saccharidic ring. Another strategy was the chemical or biochemical transformation of one or more hydroxyl groups to facilitate the introduction of the polymerizable group at that position.

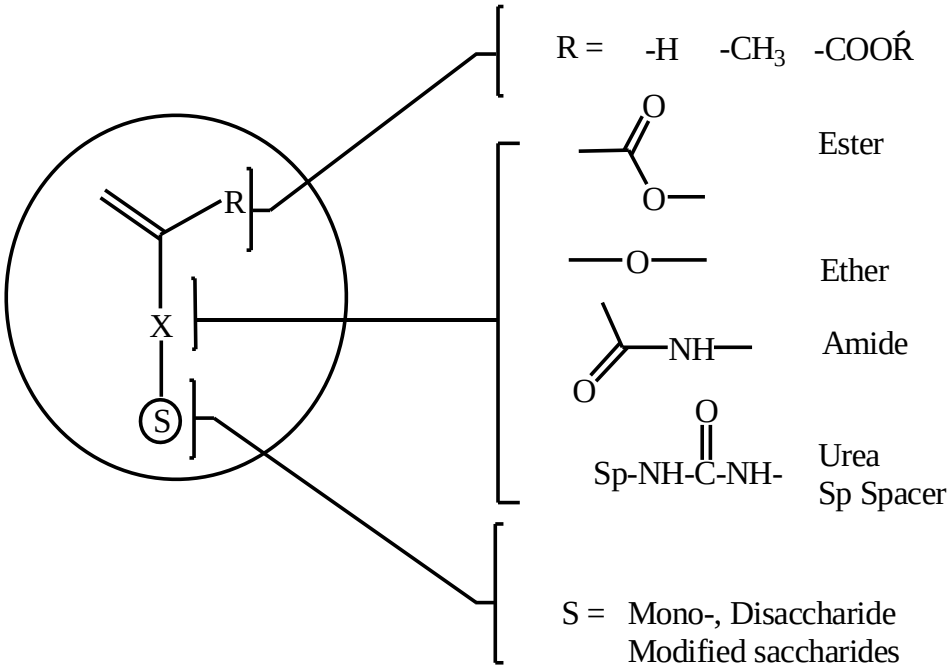
1.1.1. Vinyl sugar monomers

Scheme 1.1 shows the general chemical structure of some vinyl sugar monomers. The sugar moiety in these monomers may be mono- or disaccharides, in which the hydroxyl groups could be protected or unprotected. The polymerizable double bond may be directly connected with the saccharide unit or through spacers (X), which may be ester, amide, ether, or glucosyl groups. The direct bonding of the double bond with the sugar rest (through a carbon-carbon linkage) gives more stability to the monomer and the corresponding polymer rather than the link by spacer groups. With respect to using of protecting groups, two main classes for the saccharide based monomers can be distinguished (see below A and D).

A) Monosaccharide based monomers without protecting groups

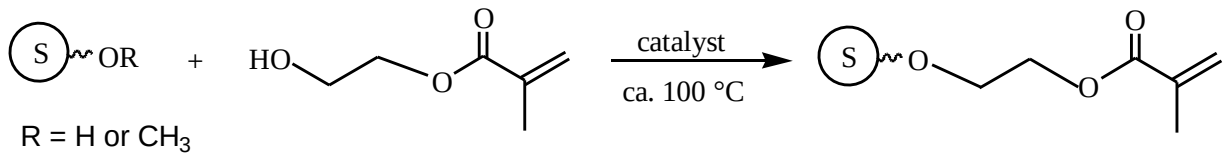
Several vinyl monomers bearing monosaccharide residues were synthesized by direct coupling of 2-hydroxyethyl methacrylate (HEMA) with some aldoses including D-glucose, D-galactose,

D-mannose, and D-xylose to form the so-called glycoside monomers (GM) as shown in scheme 1.2 [14]. All of these monomers are soluble in water but insoluble in hydrocarbons. They also easily homo- and copolymerized with a wide range of commercial monomers such as styrene, alkyl (meth)acrylates, etc. The toxicity tests showed that GM monomers are very safe material for living beings.



Scheme 1.1. The general chemical structure of vinyl saccharide monomers

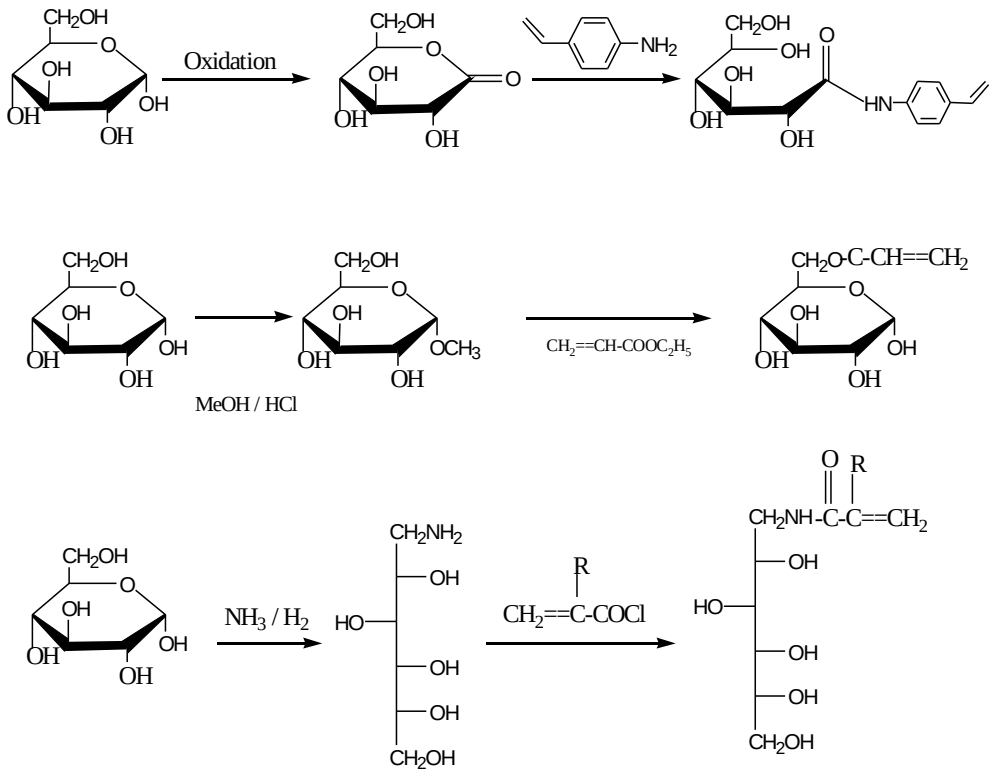
Homopolymers of GM are water soluble. Kitazawa et al. [14] reported about the syntheses and the free radical (co)polymerizations of glycoside monomers. Copolymerization of glycoside monomers with (meth)acrylates such as BA and MMA forms random copolymers and with styrene block copolymers. Moreover, it was shown that a small number of saccharide moieties were needed to make the polymers highly cohesive and hydrophilic. It was also found that GM polymer crosslinked easily by heating, irradiation or by adding crosslinking agents.



Scheme 1.2. Chemical structure of glycoside monomers (GM)

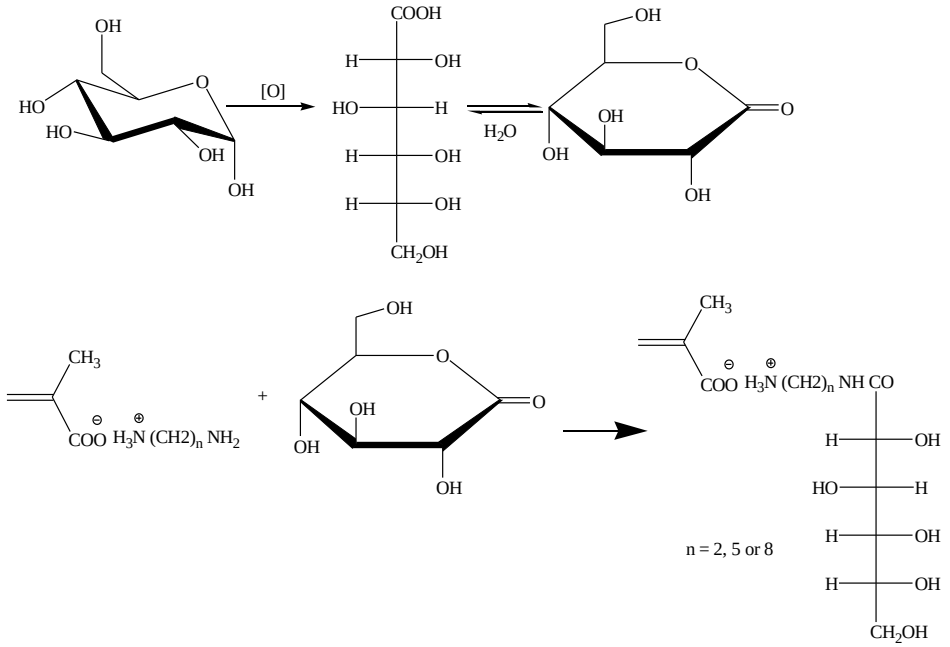
Free radical homopolymerizations of glycoside monomers were carried out in water under general conditions. The formed polymers had high molecular weight (10^5 g/mol). These

polymers are hydrolyzed gradually in strong acidic or basic medium due to the weakness of the glycosidic bond. Such polymers were also considered to be biodegradable. These glycoside based homopolymers are biological active and enhanced antigen-antibody activity in some diagnostic systems. Copolymers from GM and BA, MMA and St are water insoluble but only swelled in it. Some surface properties of these copolymers were measured. The introduction of a small amount of GM in a MMA polymer caused a large increase in wettability and the hydrophilicity of the surface.



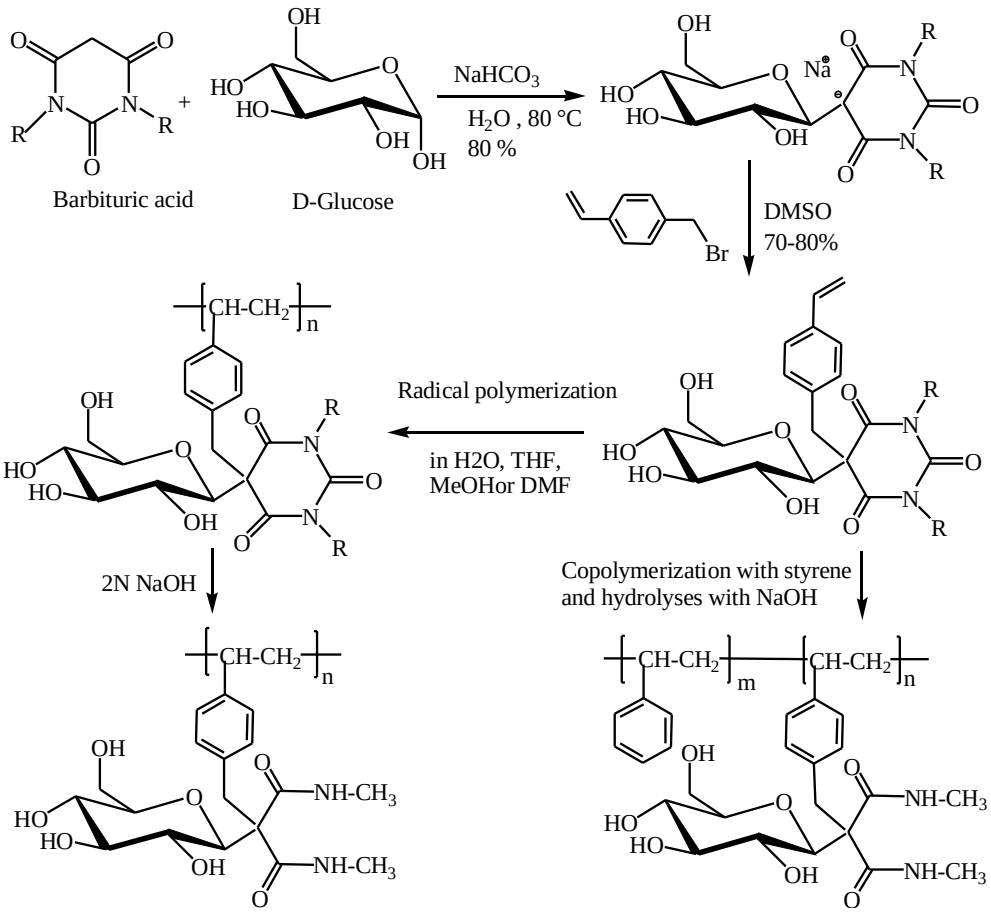
Scheme 1.3. Two steps synthesis of some saccharide monomers without protecting groups

Another strategy to prepare saccharide monomers without using protecting groups is described in scheme 1.3. Depending on the chemical transformation of the monosaccharides, the introduction of the double bond can be achieved regioselectively. Starting from D-glucose for example, a simple chemical modification such as oxidation or reductive amination of the aldehyde group, or methylation of the anomeric center, before the addition of the polymerizable group, is essential. The obtained monomers are crystalline and soluble in water. Jhurry et al. [15] reported on the synthesis and polymerization of a glucose based aminoalkylammonium methacrylate (scheme 1.4). Its radical copolymerization with vinyl pyrrolidone gives a random copolymer. The resulted water soluble copolymer was used as a coagulating agent and also as precipitating agent for divalent metals.



Scheme 1.4. Synthesis of glucose based aminoalkylammonium methacrylate monomer

The monomer described in scheme 1.5 is characterized by the direct coupling of the glucose derivative and styrene through -C-C- bonding. The final homopolymer exhibits extraordinary adsorption behavior, which expands its application chances as super absorber [16].

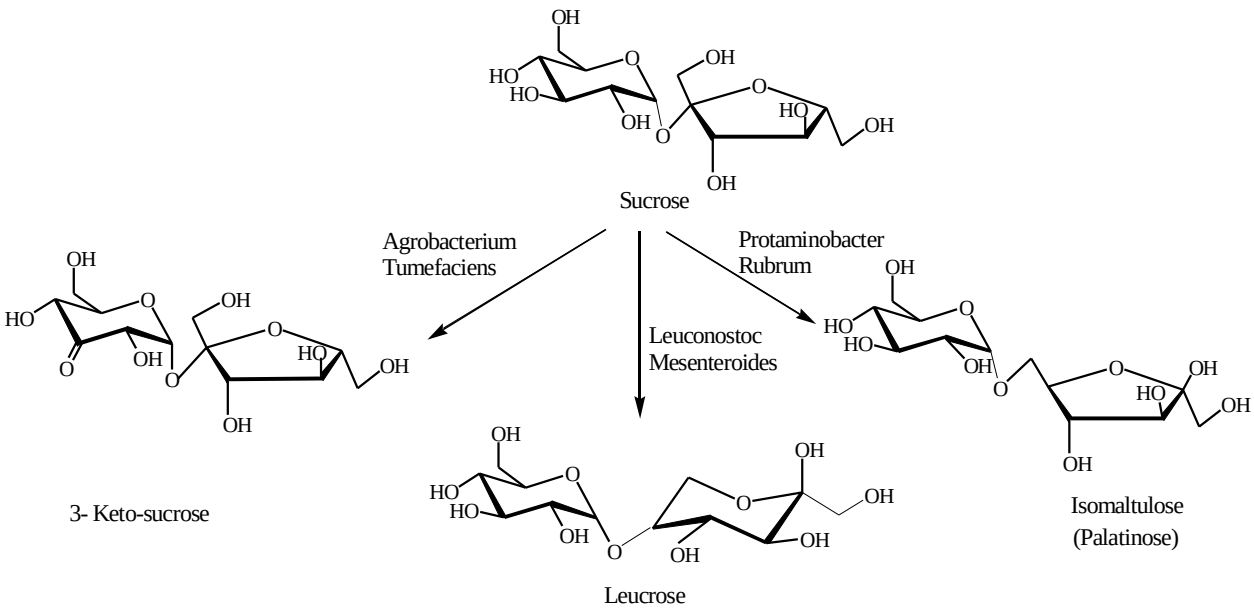


Scheme 1.5. Synthesis of styrene bearing glucose moiety and its polymerization yielding poly(styrene) bearing hydrophilic glucose derivative [16]

B) Monomers based on disaccharides

Sucrose, the most abundant disaccharide is produced yearly in millions of tons with high purity (>99.9%). Numerous attempts were conducted to prepare sucrose-containing monomers. The first attempt was carried out by direct reaction of sucrose with reactive vinyl derivatives in suitable solvents like dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), but no defined products were obtained. The degree of substitution depended mainly on the ratio of sucrose to methacrylate. Recently, Gruber et al. [17] reported on the preparation of methacryloyl sucrose and its free radical precipitation and inverse suspension polymerization. A crosslinked hydrogel was obtained and further functionalized with maleic acid anhydride or chlorosulfuric acid.

A second attempt was conducted through the introduction of a carboxylic or an amino group into the sucrose molecule. This was achieved by the formation of sucrose esters with regioselective reacting compounds, e.g. special tosylates. Then these products were transformed by replacing the leaving tosyl group by cyano or azide group and finally saponification or hydrogenation into monocarboxylic or monoaminopolyhydroxy compounds, respectively. These active sucrose derivatives were selectively substituted with vinyl reagents to give the polymerizable monovinyl sucrose. This way also did not find any industrial interest, due to the high cost and the complicated reaction pathway.

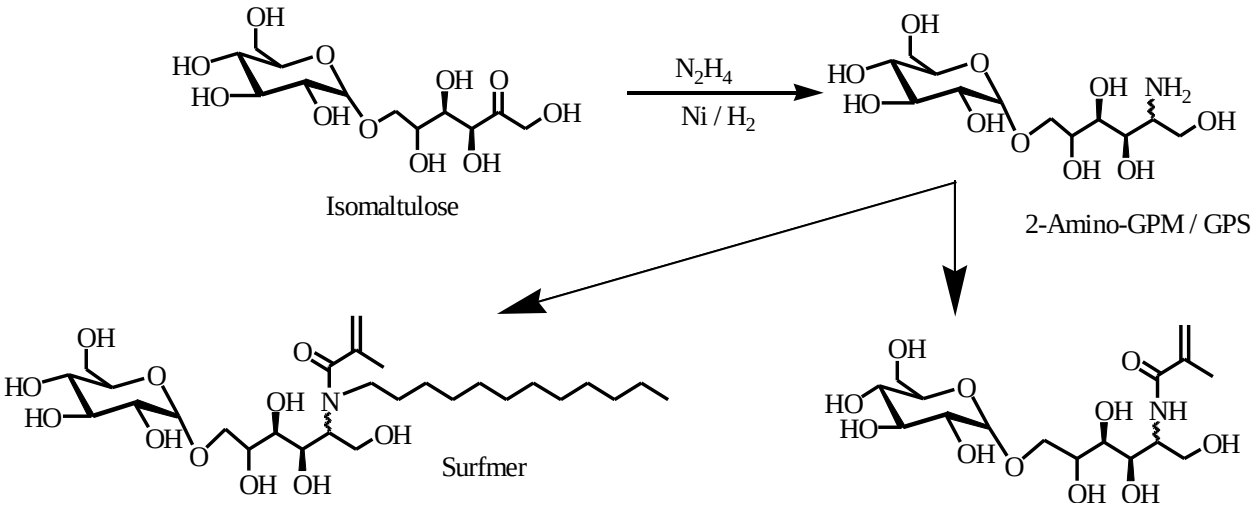


Scheme 1.6. Biochemical transformation of sucrose into reducing disaccharides.

Another way to prepare monovinyl sucrose monomer is the use of the biochemical transformation of non-reducing sucrose into reducing disaccharides, which are capable to react with vinyl derivatives yielding vinyldisaccharides. As shown in scheme 1.6, sucrose can be

transformed biochemically into different reducing disaccharides depending on the type of the microorganism.

The sucrose isomers isomaltulose, leucrose and 3-keto-sucrose can be further functionalized through oxidative cleavage, reductive amination or catalytic oxidation. Scheme 1.7 shows an example about reductive amination of isomaltulose and the preparation of monoacryloyl isomaltulose. The reductive amination was also used for monofunctionalization of other reducing mono- and disaccharides such as glucose, mannose, and lactose. Monomers with surfactant character (**surfmer**) which can be used as reactive surfactant in emulsion polymerization were prepared by the previous reaction pathway. The radical polymerization of several monovinyl saccharides and also their copolymerization with many commercial petrochemical comonomers were intensively studied by Buchholz [18], Klein [19, 20], and Kunz [21, 22]. The chemical and physical properties of these polymers were investigated and showed interesting properties.



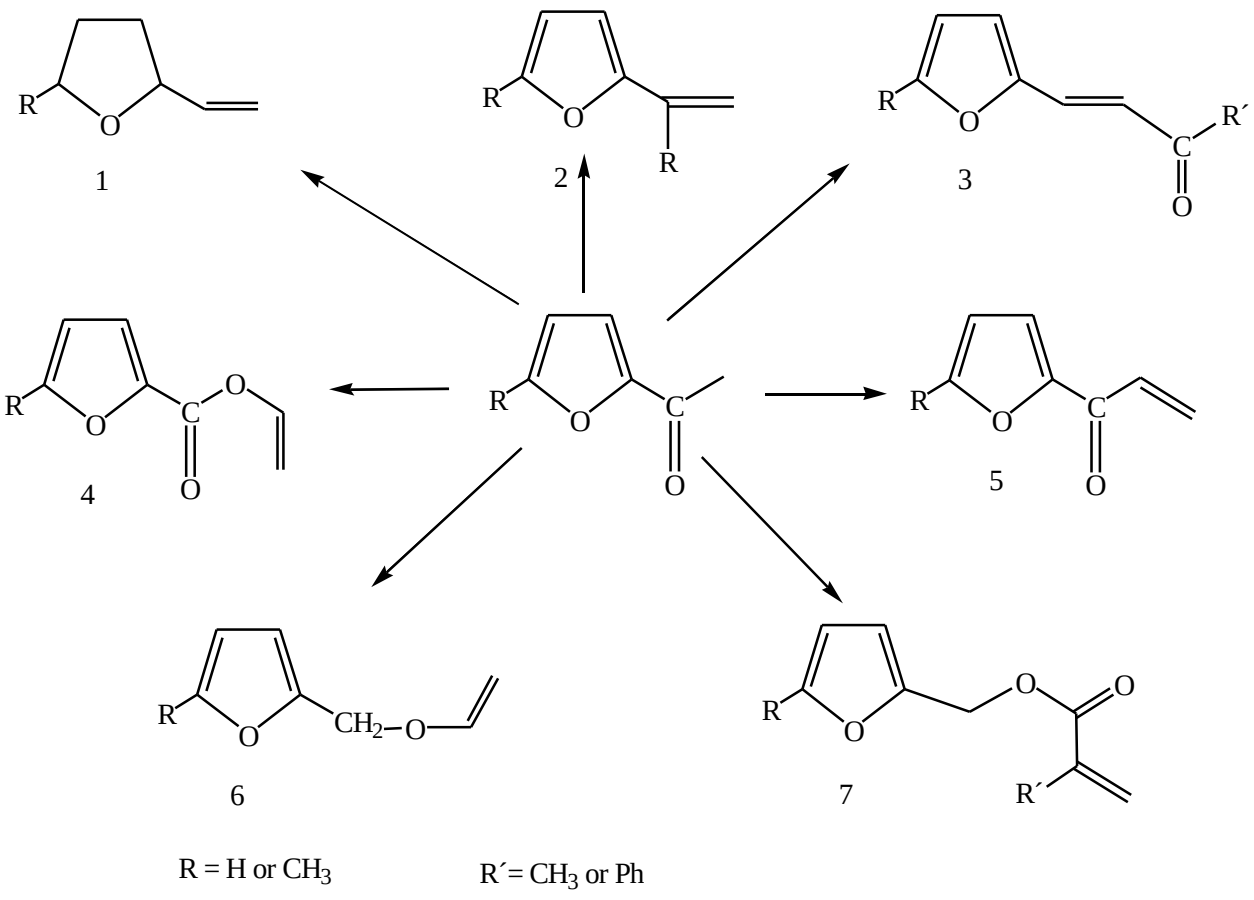
Scheme 1.7. Reductive amination of isomaltulose and synthesis of vinyl monomer derivatives.

Kurth et al. [23] has used the above described way to prepare acrylic monomer based on lactose, by means of 1-(acrylamido)-1-deoxylactitol. The radical polymerization of the later yielded a water soluble polymer which was used as a ligand for borate complexation.

C) Monomers containing a furan ring

Another interesting starting material or building block for the preparation of monomers is the 2-furanaldehyde, commonly known as furfural which can be obtained from some by-products such as sugar cane bagasse, corn cobs, paper mills and others. Gandini [24] reported about the preparation of polymers and oligomers bearing furan rings. The furfural derivatives based monomers as shown in scheme 1.8 were used for chain polymerization. The monomers depicted

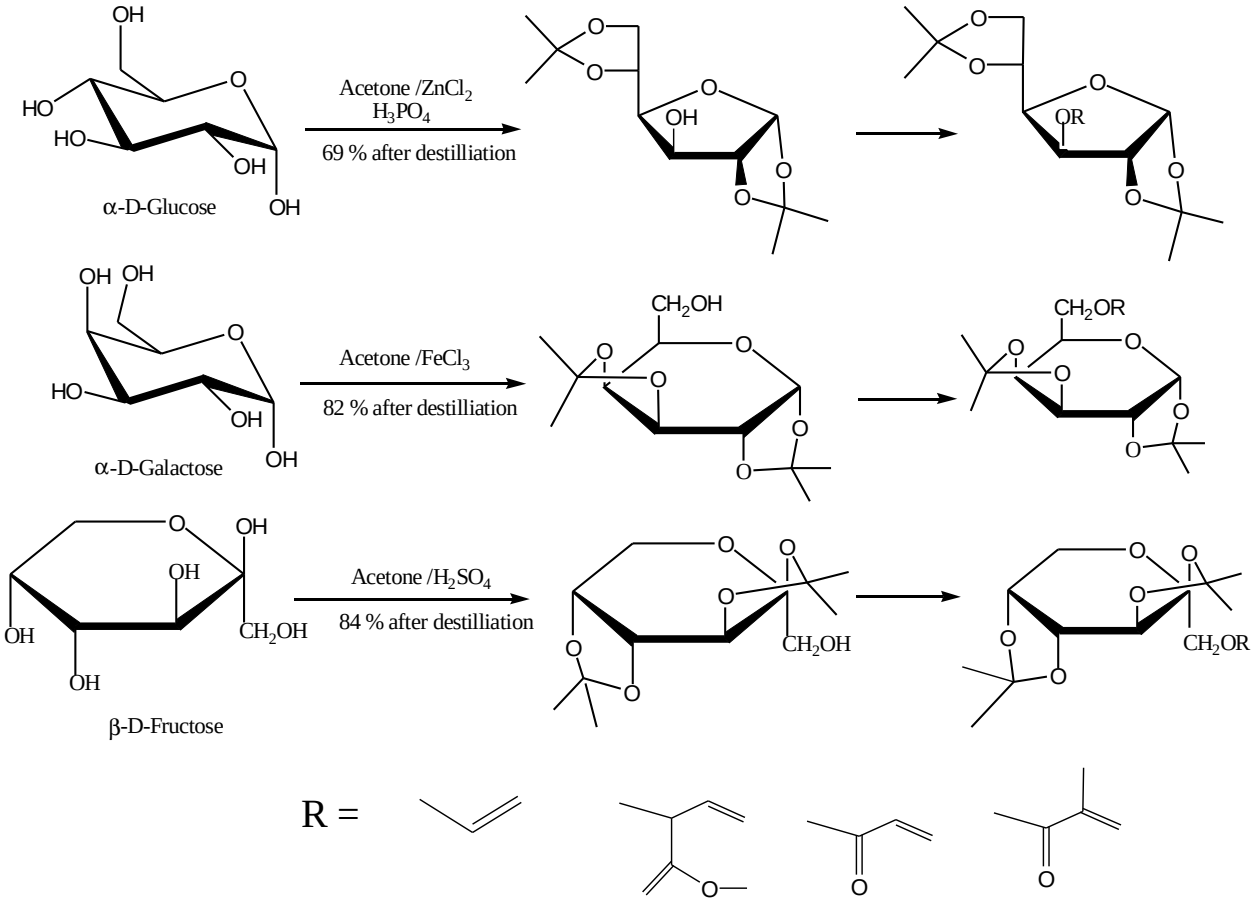
in scheme 1.8 can be initiated by free radical, cationic and anionic initiators. The free radical may be added to the external double bond or added to the C5 position of the furan ring to give the furyl radical. The second possibility complicated the polymerization due to the stability of the free radical through the furan ring (mesomeric effect). 2-vinyl furanoate (4) does not polymerize under standard condition of free radical polymerization because the initiation takes place at C5. In contrast, 2-furfuryl methacrylate (7) polymerizes readily without complications. 2-vinyl furan (2) displays an intermediate behavior in that it polymerizes slowly, but gives modest degree of polymerization and limited yields. In copolymerization, the 2-vinyl furanoate inhibits the polymerization of vinyl acetate, acrylonitrile, and styrene, but does not interfere with the polymerization of methyl methacrylate, although it is not incorporated in the polymer. 2-furfuryl methacrylate copolymerizes with styrene and MMA giving high conversion and high molecular weight. In conclusion, the behavior of furanic monomers in (co)polymerization depends on the degree of stabilization of the initiated radical.



Scheme 1.8. Various monomer types based on 2-furanaldehyde (furfural)

D) Preparation of sugar monomers by the use of protecting groups

As we have pointed previously, the use of the protecting group strategy facilitates the regioselectivity of monosubstitution of the saccharide moieties in a specific position. The most common protecting groups for hydroxyl groups are esters, ethers, and acetals. Due to the special reactivity of the anomeric hydroxyl group in carbohydrates, it is usually protected prior to all other hydroxyl groups. Fischer glycosylation or the acid catalytic hemiacetal of saccharides with alcohol is a simple way to protect the anomeric OH-group. The protection mechanism, sometime takes place in several steps [25]. From an industrial point of view it is important that, the protecting groups are not expensive and the protection steps are as few as possible.

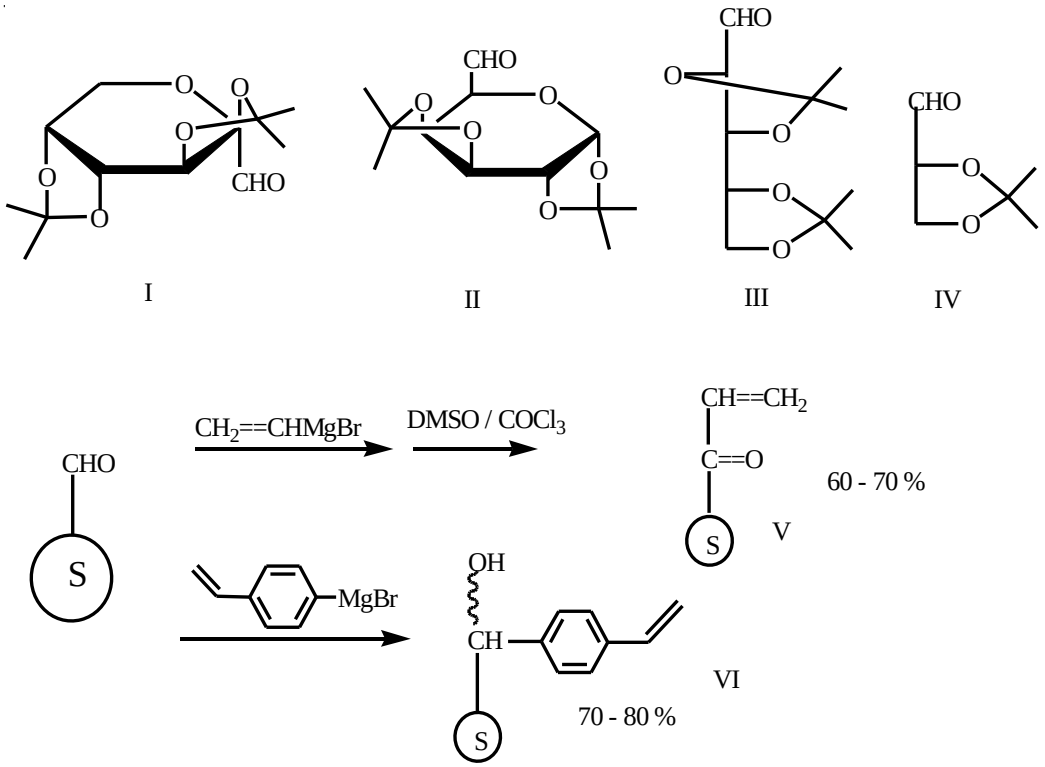


Scheme 1.9. Preparation of some vinyl sugar monomers with the protecting group strategy.

The selection of the protecting group, by means of the stability and the release ability, depends on the end use of the materials. Isopropylidene acetals are the cheapest protecting groups and are often used for the protection of *cis*-positioned 1,2-diol groups in saccharides. Scheme 1.9 shows the one step synthesis of diisopropylidene derivatives of D-glucose, D-galactose and D-fructose. The activation of the last free hydroxyl group via different polymerizable double bonds (second step) leads to the corresponding monomers. H. van Grunenberg et al. [26] reported in 1939 on the preparation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (DAG). The introduction of

an acrylic, methacrylic or allylic group to such diisopropylidene derivatives was frequently used. In 1960, Black et al. reported about the preparation of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG) [27]. Some optimizations on this reaction have been reported. The free radical (co)polymerization of such monomers in bulk and solution was intensively studied in the last decades [27-33]. 3-MDG was first polymerized in emulsion polymerization by Klein et al. [38] in order to obtain a high molecular-weight polymer. The deprotection of the isopropylidene groups of 3-MDG through acid hydrolysis of the precipitated polymer, gives water soluble polymer [poly(3-MG)] with interesting applications for oil recovering. Then 3-MDG was intensively investigated in batch emulsion homo- and copolymerization by Yaacoub et al. [34-37].

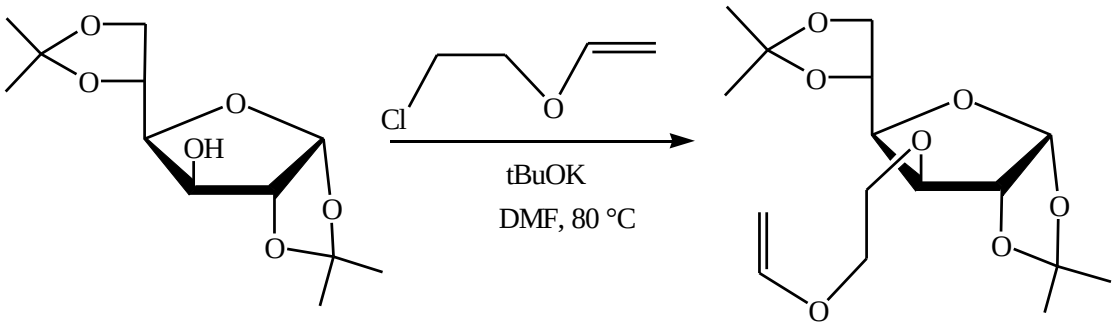
Scheme 1.10 shows two sugar based monomers with polymerizable double bonds which are directly connected with the saccharide moieties.



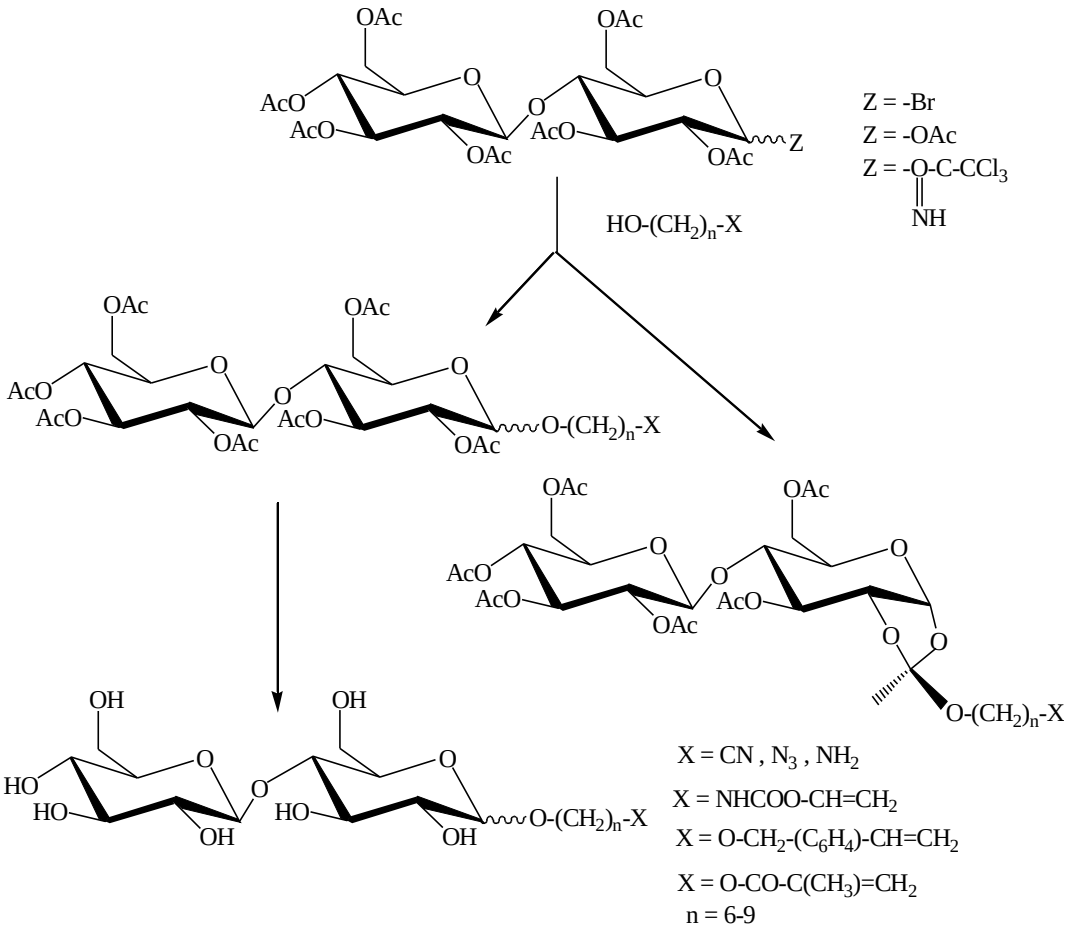
Scheme 1.10. Vinyl sugar monomers through (-C-C-) bond with a polymerizable group.

The aldehyde group of diisopropylidene derivatives (I-IV) was treated with vinyl magnesium bromide in DMSO/$COCl_2$ or 4-styryl magnesium bromide to give the corresponding monomers (V and VI). A more easier way is the starting with D-glucolactone with diethyl amine in acetone/H^+ in a one pot reaction to give diisopropylidene glucamine, which can be directly reacted with vinyl magnesium bromide to give a vinyl saccharide. Deffieux et al. [39] reported the synthesis of a glycosidic vinyl ether monomer (scheme 1.11) and it's copolymerization with

styrene. Amphiphilic block copolymers were obtained by deprotection of the sugar moieties after the polymerization. Barros et al. [40] reported the syntheses of optically active monomers and copolymers derived from protected 6´-*O*-acryloyl sucrose. The monomers were synthesized by a multi-step route (about 5 steps). Chiral copolymers were prepared from these monomers with styrene and MMA.



Scheme 1.11. Preparation of glycosidic vinyl ether monomers.



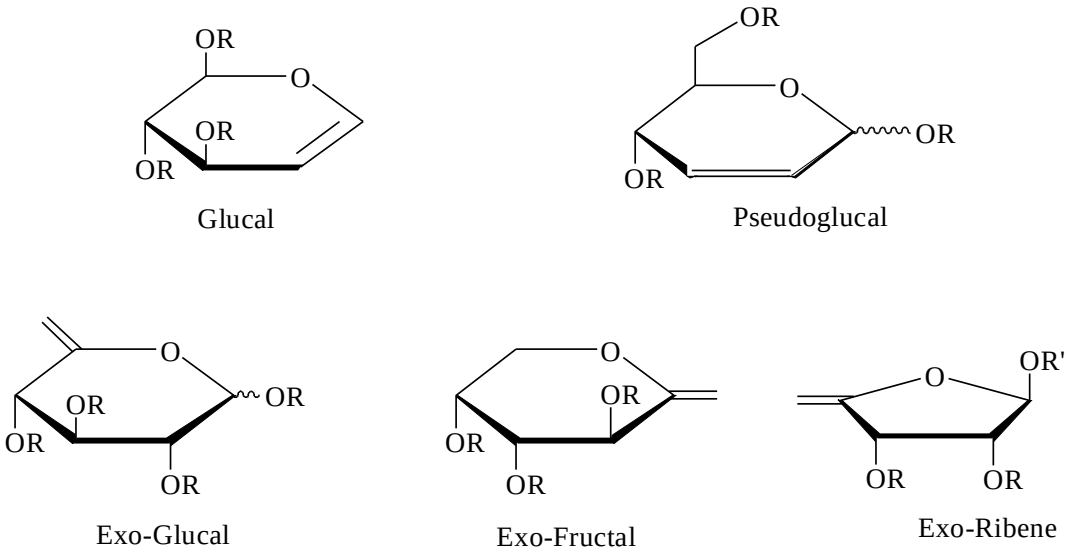
Scheme 1.12. Schematic representation of the various steps for the preparation of cellobiose based monomers

Pichot et al. [41] reported the synthesis of hexyl methacrylate-terminated cellobiose monomers starting from 2,2´,3,3´,4,6,6´-hepta-*O*-acetyl-α-D-cellobiosyl bromide through a five steps procedure (scheme 1.12). Kinetic of radical polymerization in dimethyl sulfoxide was studied. Copolymerization with styrene was investigated. A preferential syndiotactic configuration was clearly evidenced in the homopolymer.

1.1.2. Unsaturated sugar monomers

The double bond can be produced by the dehydration of a monosaccharide to give the so-called unsaturated sugars. These unsaturated sugars have different structures from the well-known vinyl sugar monomers. The polymerizable olefinic double bound can be in “endo” or “exo” cyclic position of the pyranoid (six-membered ether ring) or furanoid (five-membered ether ring) structure of the monosaccharide derivatives involving several positions of the sugar ring. Buchholz et al. [42] and Yaacoub [43] optimized the preparation of several unsaturated sugar monomers such as exo-ribene, exo-fructene and exo-glucal based on D-ribose, D-fructose, and D-glucose, respectively. The free radical polymerization of these monomers was studied. Scheme 1.13 shows the chemical structure of some unsaturated saccharide monomers. These monomers are water soluble, if R= H, or water insoluble, if R = acetyl, benzoyl, benzyl, methyl or isopropylidene group. The radical copolymerization of these unsaturated saccharide monomers with commercial comonomers such as N-vinyl pyrrolidone (NVP), methyl methacrylate (MMA), and styrene (St) was carried out in bulk and in solution. Water was used as polymerization medium in case of water soluble monomers and organic solvents for water insoluble monomers. The bulk homopolymerization of exo-ribene was conducted at high temperature (130 °C) and the produced homopolymer exhibited low molecular weight (ca. 2800 g/mol).

Exo-ribene was copolymerized with many vinyl comonomers such as NVP, vinyl acetate (VAc), MMA, and MA at 80 °C. The corresponding copolymers had high molecular weights in the range of 1 to 5 $x10^4$ g/mol. Pseudoglucal was copolymerized with NVP, MMA and St at 60 °C in toluene for 48 h with 1% AIBN as initiator. The polymerization yields were about 20-35% and the copolymers had relatively high molecular weights (1.7-7.8 x 10^4 g/mol). The copolymers contained less pseudoglucal (5-25%) than the initial monomer composition (50/50%).



Scheme 1.13. Some unsaturated sugar monomers

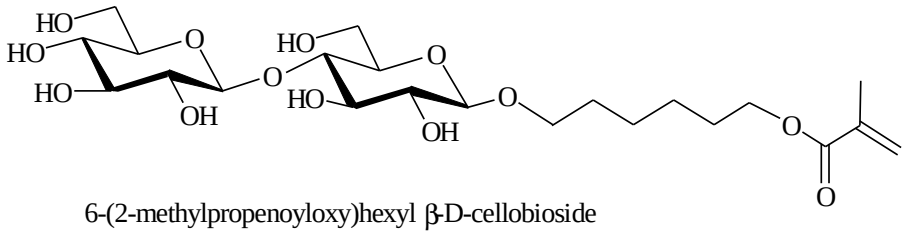
Exo-glucal copolymerized well with maleic acid anhydride (MAh), MA and MMA. High yields were obtained (32-63%). An alternating copolymer was obtained with MAh. Benzolylated exo-fructal was polymerized at 120 °C and led to a homopolymer with high molecular weight (6 x 10^4 g/mol). It gives an alternating copolymer with MAh with high M_w of 10.6 x 10^4 g/mol. These new polymeric materials could find applications in the field of cosmetics, pharmaceutics, paints and coatings and adhesives.

1.1.3. Emulsion polymerization of some saccharide monomers

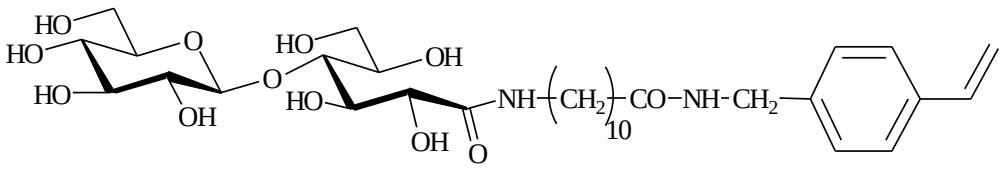
Emulsion polymerization is a widely used industrial polymerization process, due to its advantages over the other polymerization techniques. So, several papers have dealt with the preparation of polymer latexes containing saccharide residues. Black et al. [44] reported in 1968 about the emulsion copolymerization of 6-*O*-acryloyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (3-ADG) with MA. The authors reported that the bulk copolymerization of 3-ADG and MA under free radical conditions was a violent exothermic reaction. So, they have used the emulsion process in order to control the heat of polymerization. The yield of copolymerization was over 90 % and the copolymer exhibited only one glass transition temperature (T_g). The copolymer was optically active due to the galactose moieties and the optical activity was depending on the copolymer composition. The deacetonation or the deprotection of this copolymer was carried out by dissolving the copolymer in acetone, formic acid and water at 20 °C for three days. The hydrolyzed copolymer was insoluble in acetone-water mixture but soluble in dimethylformamide. The T_g of the deprotected copolymer was about 4 °C higher than the value of the original copolymer (25 °C) and the optical activity increased from -15 to +17 °.

In 1985 Klein et al. [38] reported on the free radical emulsion polymerization of 3-MDG. The aim was the preparation of high molecular weight water-soluble polymer containing saccharide moieties. The deacetonation of poly(3-MDG) was achieved by using formic acid aqueous solution. The formed water soluble polymer had a molecular weight in the range of 10^6 g/mol.

At the beginning of 1990, Pichot et al. [45, 46] had used surface active saccharide monomers in order to functionalize the surface of polystyrene latex particles. The aim of this functionalization was the control of the hydrophobic-hydrophilic balance at the water polymer interface in order to use it in the diagnostic tests. Surface functionalization by saccharide moieties is favorable due to their biocompatibility as well as their role in some recognition processes. Scheme 1.14 shows two saccharide monomers, used for the functionalization of poly(styrene) latex. Such monomers have surface activities and act as emulsifier. The saccharide moieties present the hydrophilic part and the alkyl chains the hydrophobic part. The incorporation of these surfmers (surface active monomers) on the surface of polystyrene particle was achieved by seed polymerization.



6-(2-methylpropenoyloxy)hexyl β-D-cellobioside



11-(N-p-vinylbenzyl) amido undecanoyl maltobioamide

Scheme 1.14. Two surface active saccharide based monomers used for the functionalization of styrene seed latexes.

In recent years, Yaacoub et al. [34-37, 47] reported on the emulsion polymerization of some saccharide monomers with the following aims:

1) Use of water insoluble saccharide monomers as a main component and not as additives in latex formation in order to obtain hydrophobic saccharide based latexes.

2) Preparation of functionalized latexes with defined morphology such as core-shell morphology by using water soluble saccharide monomer as well as saccharide surfmers.

The authors used different polymerization techniques such as batch, semicontinuous and multistage emulsion polymerization and the miniemulsion technique to prepare the so-called sugar latexes.

Nevertheless all the previous attempts, the syntheses and large scale preparation of saccharide based monomers are still in the immature phase. Until now, there is no sugar monomer commercially available produced in an industrial scale and this could be related to many factors:

- The preparation of monomers bearing a saccharide moiety is in general complex and requires several steps, especially in the case of monosubstituted monomers.
- The prices of the petrochemical monomers are considerably lower.
- The properties of these new polymeric materials are well studied, but the advantages of these materials over the traditional ones have not yet been investigated thoroughly.
- The industry didn't take the initiative to produce such new polymers.

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1.2. Emulsion Polymerization

The polymerization techniques can be classified according to the polymerization medium into two main classes, homogeneous and heterogeneous polymerization. In homogeneous polymerization such as bulk and solution polymerization, the monomer (a solvent) and the initiator are present in one phase. In contrast, in heterogeneous polymerization there are usually two immiscible phases (more than one phase) and it can be subdivided into four techniques:

i) Precipitation polymerization is usually performed in organic solvents or in water, which are good solvents for the monomers and poor solvents for the polymer formed using either an oil-soluble or water-soluble initiator. The polymer can be stabilized in the medium in the presence of a dispersing or stabilizer agent.

ii) Dispersion polymerization is polymerization in which the monomer, initiator, and surfactant are soluble in a supercritical fluid such as CO_2. The main advantage of this technique is that at the end of the polymerization, the medium readily evaporate by opening the reactor and the formed spherical polymers are easily isolated without further purification.

iii) Suspension polymerization involves the dispersion of hydrophobic monomer(s) as droplets in the continuous water phase using dispersing agents. Polymerization is performed using an initiator soluble in the monomer droplets with a size of ca. 10-100 µm. In each dispersed droplet, the radical polymerization follows the bulk polymerization kinetics. The average size of the end particles (gel or macroporous resins) is in the range of 20 µm to a few millimeters.

iv) Emulsion polymerization is usually obtained by emulsifying a water-immiscible monomer in an aqueous medium containing an O/W emulsifier. The polymerization is generated preferentially using a water-soluble initiator. The monomer droplets before the polymerization are commonly in the range 1-10 µm, whereas the final latex particles size is in the submicron range.

Inverse emulsion polymerization is a system prepared usually by emulsifying a water-soluble monomer in a continuous organic phase with a W/O emulsifier. An oil-soluble or water-soluble initiator is used to initiate the polymerization to form latex with size in the domain 50-300 nm.

We will focus the light on the emulsion polymerization. Emulsion polymerization is classified according to colloidal stability and size of the end polymer particles into three classes; mini-, micro- and macro-emulsion.

Macroemulsion polymerization or commonly named classical or conventional emulsion polymerization as defined before is performed by emulsifying a monomer in water by using O/W emulsifier to form a monomer droplets with size in the range 1-10 µm. The polymerization is

carried out usually by using the free radical technique and the end latex has a size in the range of 50-1000 nm, which depends on many parameters such as the concentration and the type of the emulsifiers, the initiators and all other additives, the polymerization temperature and the stirrer diameter and speed. The macroemulsion system prior to the polymerization is kinetically stable; this means it is only stable under stirring.

Miniemulsion polymerization is performed by application of high shear force on a system consisting of a monomer, water, emulsifier and a coemulsifier or hydrophobe (very highly hydrophobic agent) such as hexadecane or cetyl alcohol. The miniemulsions are thermodynamically unstable and are therefore only stable for a limited period of time, ranging from hours to days. The monomer droplets are in the range of 50-500 nm and the polymerization proceeds within these droplets either using oil-soluble or water-soluble initiator.

Microemulsion polymerization is thermodynamically stable. It is prepared by high shear rates or by increasing the emulsifier concentration. The monomer droplets are in the range of 10 to 50 nm.

1.2.1. Mechanisms of conventional emulsion polymerization

The mechanism of emulsion polymerization has been extensively studied by many authors. The first quantitative theory of the emulsion polymerization was written by Harkins [1] and then modified by Smith and Ewart [2]. More recent contributions were given by Ugelstad and Hansen [3], Gardon [4, 5], Gilbert and Napper [6-8], Blackley [9], Gilbert [10], and Lovell and El-Aasser [11]. Now it is widely accepted that the emulsion polymerization proceeds in three distinct intervals:

- **Interval I** (nucleation stage) is the initial stage, where particle formation takes place. The particle number and particle size usually increases (in the range of 0-10% conversion). Several mechanisms of particle nucleation have been proposed, depending on the reaction conditions (Figure 1.2.1).
- **Interval II** (growth stage) begins when the nucleation of particles is completed. It is characterized by the disappearance of the micelles, a constant number of particles and an increase in particle size. This stage corresponds to a conversion range of 10-40%.
- **Interval III** (depletion stage) begins with the disappearance of monomer droplets, after which the monomer concentration in the particles and in the water phase starts to decrease continuously with the conversion (in the range 40-100%).

1.2.1.1. Nucleation mechanisms

1. Micellar nucleation: Using emulsifiers over their critical micelle concentrations (CMC), Harkins proposes in his qualitative theory the micelles as the locus of nucleation. Radicals originated in the aqueous phase are postulated to enter into the micelles, then forming particle nuclei. Polymerization proceeds from the monomer supplied by the monomer droplets by diffusion through the aqueous phase. Stabilization of the growing particles is ensured by the emulsifier molecules provided with the uninitiated micelles. This stage ends with the disappearance of the empty micelles. The micellar nucleation mechanism generally concerns sparingly water-soluble monomers, which are also miscible with their polymers, and provide emulsifier concentration above the CMC. It applies to monomers like styrene, butadiene, n-hexyl acrylate, vinyl toluene, etc. This nucleation mechanism has been elegantly quantified by Smith and Ewart. However, this theory can be strictly applied only for batch polymerization process and for hydrophobic monomers, but unable to explain various phenomena observed in the case of polar monomers (such as vinyl acetate, vinyl chloride, acrylonitrile, methyl methacrylate, etc.) with larger water solubility than styrene. Other arguments against this theory were the possibility to prepare latex at low emulsifier concentration (below CMC) or without using an emulsifier. These observations called for alternative models for nucleation.

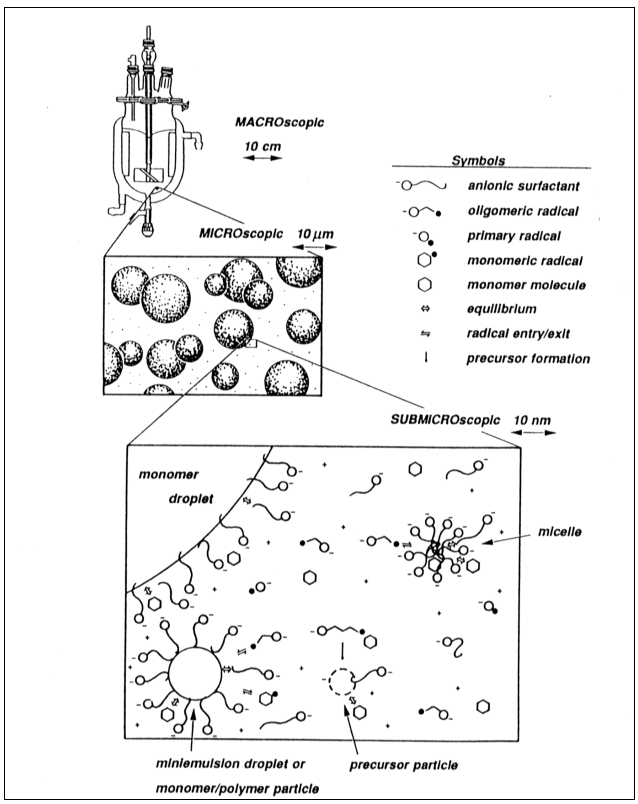

Figure 1.2.1. Schematic presentation of the early stages of emulsion polymerization ([11], p. 702).

2. Homogeneous nucleation: The homogeneous nucleation was proposed by Fitch and Tsai [12] and extended by Hansen and Ugelstad [3]. This theory is well known as the so-called HUFT-theory. Free radicals react in the aqueous phase with solubilized monomer to form growing oligomeric radicals. These species propagate until they reach a critical length, in which their solubility in the aqueous phase attained a limit. These surface active oligomeric radicals due to the sulfonate end group generated from the dissociation of the persulfate initiator, either precipitates or form micelles to form a primary particle. This model can explain the nucleation in case of emulsifier-free emulsion polymerization and can also applied to explain vinyl acetate and vinyl chloride emulsion polymerizations, exhibiting water solubility much higher than styrene (290 and 170 mmol respectively). Briefly, the quantitative HUFT-theory takes in consideration three main points. The rate of particle nucleation can be related to the rate of radical generation in the aqueous phase (R_i), the rate of oligoradical capture by existing particle (R_c) and the rate of flocculation of polymer particles (R_f).

$$dN/dt = R_i - R_c - R_f \quad (1)$$

It is postulated that the rate of particle formation is equal to the rate of free radical generation in the aqueous phase. An efficiency factor (b) was introduced to compensate the termination reaction in aqueous phase.

$$dN_p/dt = R_i = b\,(2\,f\,k_d\,[I]) \quad (2)$$

where f, is the initiator efficiency, [I] the initiator concentration, k_d the decomposition rate constant of initiator. Some oligomers are captured by other formed particles and that reduced the rate of particle formation.

$$dN_p/dt = R_i = b\,(2\,f\,k_d\,[I]) - R_c \quad (3)$$

Moreover, a flocculation process may take place between two formed particles to improve the colloidal stability thought the increasing of the surface charge density according to the Van der Walls attractive forces.

$$dN_p/dt = R_i - R_c - R_f \quad (4)$$

After a period of time, a steady state is reached. If the time to reach this state is short, then all the particles will grow at the same average rate and monodisperse latex will be obtained. If the reverse is true, polydisperse latex will be formed.

3. Coagulative nucleation: Napper and Gilbert [6-8] proposed that the particle formation takes place via two steps. A first step involves the simultaneous formation of precursor particles either by homogeneous or micellar nucleation. These precursors have extremely small size and tend to coagulate to form stable colloids, the so-called mature particles. The coagulation events involved in the nucleation mechanism explain the maximum in the particle numbers in interval I for

systems without or with low emulsifier content or with highly water-soluble monomers. This model predicts a dissymmetric particle size distribution at the end of the nucleation step.

In conclusion, it is difficult to determine a general nucleation mechanism but it can be predicted according to the emulsion polymerization characteristics such as the type and the water solubility of the monomer and initiator, the temperature, the propagation rate constant, and importantly the emulsifier type and concentration. The dominant nucleation mechanism for polymerization systems below the CMC is the homogeneous coagulative mechanism, although micellar nucleation cannot always be completely ruled out. For a system above the CMC, it can involve all the three types of nucleation mechanisms, especially for polar monomers. However, the micellar model often dominates.

1.2.1.2. Particle growth

As pointed out before, the particle growth is the second step in the emulsion polymerization and it begins when the nucleation of particles is completed. It is characterized by the disappearance of the micelles, a constant number of particles and an increase in particle size. This stage corresponds to a conversion range of 10-40%. In this stage the overall polymerization rate (R_p) is constant, because the number of particles as well as the concentration of monomer within the polymer particle is constant.

The basic rate equation for homogeneous batch free radical polymerization is

$$R_p = -\frac{d[M]}{dt} = k_p\,[M]\,[R^\bullet] \qquad (5)$$

where R_p is the rate of polymerization per unit volume, k_p the propagation rate constant, [M] the monomer concentration, and $[R^\bullet]$ the radical concentration. In the emulsion polymerization the main loci of polymerization are the particles; thus the rate equation must contain the number of particles N_p as well as the concentration of monomer and the radical in the particle, leading to

$$R_p = \frac{k_p\,\bar{n}\,[M]_p\,N_p}{N_A} \qquad (6)$$

where $[M]_p$ is the monomer concentration in the particle, $\bar{n}$ is the average number of radicals per particle, N_p the total number of particles per unit volume, and N_A the Avogadro's number. The time evolution of the fractional conversion in a batch process, x is then

$$\frac{dx}{dt} = \frac{k_p\,[M]_p\,N_p}{N_A\,n_{m0}}\,\bar{n} = A\,\bar{n} \qquad (7)$$

where $A = K_p\,[M]_p\,N_p/\,N_A\,n_{mo}$ and n_{mo} is the initially added number of moles of monomer per unit volume. Equation 6 is valid for intervals II and III.

The value of $\bar{n}$ (the average number of radicals per particle) is determined by three processes, namely: 1) absorption of radicals from the water phase into particle; 2) desorption of radicals from the particles; and 3) bimolecular termination of the radicals in the particles. Smith and Ewart presented three limiting cases determined by the ratios of entry, exit, and terminations of radicals:

Case 1: $\bar{n} << 0.5$; this indicates a high desorption rate of the radicals and the termination reaction exclusively occurs in the aqueous phase. This is the case for small particle size emulsion and for monomers such as vinyl acetate and vinyl chloride.

Case 2: $\bar{n} = 0.5$; In this case the rate of radical exit is equal to rate radical entry and the termination reaction is much faster than the propagation one. This means that one particle can accommodate 1 or 0 growing radical (the so-called 0-1 theory).

Case 3: $\bar{n} >> 0.5$; In this case the rate of radical entry is higher than the rate of radical exit. This means that more than one radical exists in the particle at the same time without fast termination reaction. It happens usually if the particle size is large and the termination rate constant is low. This case may be applied to the polymerization of acrylic monomers exhibiting gel effect. The experimental quantification of $\bar{n}$ helps to explain many features of emulsion polymerization such as the rate of polymerization, the molecular weight and molecular weight distribution of the produced polymer, and the particle size and particle size distribution of the formed latex, etc.

1.2.1.3. Depletion stage

This stage begins with the disappearance of monomer droplets. In this last stage of polymerization, the rest of monomer is mostly within the polymer particles. Its concentration in the particles and to a lower extent in the water phase starts to decrease continuously with the conversion (in the range 40-100%). This stage is less important in most cases, because the polymerization occurs in the swollen polymer particles.

1.2.2. Emulsion copolymerization

Most of the industrially produced latexes are copolymers for practical purposes. For bulk and solution polymerization, the copolymer composition equation (eq. 8) can be applied directly. However, for emulsion polymerization, the situation is more complex due to the heterogeneous nature of the reaction. Besides the reactivity ratios, the water solubility of the monomers and the partitioning of the monomers between the different phases of the system (water, monomer droplets and the polymer particle) play a significant role in the copolymerization.

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \quad \text{and} \quad F_B = \frac{r_B f_B^2 + f_B f_A}{r_A f_A^2 + 2 f_B f_A + r_B f_B^2} \tag{8}$$

where, f_A is the mole fraction of monomer A in the initial monomer mixture and f_B is the mole fraction of monomer B in the mixture (f_B = 1- f_A). F_A and F_B are the mole fraction of monomer A and B in the copolymer respectively. r_A and r_B are the reactivity ratios of monomer A and B respectively. They can be defined as follow;

$$r_A = \frac{k_{AA}}{k_{AB}} \quad \text{and} \quad r_B = \frac{k_{BB}}{k_{BA}} \tag{9}$$

The monomer concentration in the polymer particles determines the rate of polymerization, while the monomer ratio in polymer particles determines the chemical composition of the copolymer formed. Some authors used the thermodynamic model of Flory-Huggins for solution polymerization [13] in order to account or predict the partitioning of the different monomers between the organic and the aqueous phases [14-16].

A special aspect of the batch emulsion copolymerization is the occurrence of a composition drift in the microstructure of the copolymers [17-20]. This drift in composition can be related to the difference in the reactivity ratios of the monomers and their composition ratio in the polymerization loci (polymer particles). Many widely used emulsion systems such as butyl acrylate/vinyl acetate, styrene/butyl acrylate, styrene/acrylonitrile, show such a composition drift. The question is: how can a homogeneous copolymer composition in emulsion polymerization be obtained? Semicontinuous emulsion polymerization process was used for a long time to prepare more homogeneous copolymers. Nowadays, most of emulsion copolymers are industrially produced by this process.

1.2.3. Emulsion polymerization processes

Batch, semicontinuous, and continuous processes are the main types for carrying out an emulsion polymerization. We will spot the light on the semicontinuous technique as industrially widely used process.

In batch process all the reactants are completely added to the reactor at the beginning of the polymerization. The batch technique is the simplest one and is used more in academic studies. The free radical polymerization is high exothermic reaction and it is very difficult to control the released heat. Furthermore, the variable parameters in the batch process are very limited and there is no good control of the properties of the formed latexes and the corresponding polymers.

1.2.3.1. Semicontinuous emulsion polymerization

In this process, a part of the total reaction formulation is introduced at the beginning of the polymerization and the remainder part is added during the course of the polymerization. The technique is widely used, both industrially and in academic laboratories [17, 21-42].

Types of semicontinuous processes

There are different addition strategies to carry out the semicontinuous emulsion polymerization. Two main processes can be distinguished.

Monomer feed addition: the monomers are added, together or separately, to the reactor solely in a predetermined manner via a metering pump. In the most cases the reactor is charged with the emulsifier, water, part of the initiator, and eventually with a small part of monomer. The rest of monomer as well as the initiator are added separately.

Pre-emulsion addition: in this case the monomers are pre-emulsified with a part of water and the emulsifier to form the so-called pre-emulsion, which is then added to the reactor co-currently with the initiator. Here also, the rest of the recipe (water, emulsifier, initiator, and other additives) is added at the outset of the polymerization.

With respect to the monomers addition rate, two main conditions can be distinguished.

1. Starved feed condition: the monomers addition rate is lower than the maximum attainable polymerization rate (determined in batch process).

2. Flooded feed condition: the addition rate of the monomers is higher than the rate of polymerization.

Advantages of the semicontinuous process over the batch process are:

A) Control of the particle size and particle size distribution

B) Control of the rate of polymerization

C) Control of the heat of the polymerization

D) Control of copolymer composition

E) Control of the molecular weight and molecular weight distribution

A) Control of the particle size and particle size distribution

The particle size and the particle size distribution are important physical characteristics for an emulsion, which significantly affect the physical and mechanical properties of the system. In the batch emulsion polymerization, several of parameters can affect the particle size and particle size distribution such as the type of monomer(s), the type and the concentration of the initiator and the emulsifier, the polymerization temperature, agitation speed, stirrer diameter, the

monomer/water ratio, and others. It was also found that the number of particles (N), particle diameter (D) and particle size distribution (PSD) are varied depending on the polymerization process (i.e. the monomer addition (M), pre-emulsion addition (E), or the batch (B) process. These parameters typically vary according to:

$$N_M > N_B > N_E \qquad D_E > D_B > D_M \qquad PDS_E > PDS_M > PDS_B$$

This observation is not always the case; the above sequence depends also on the way of addition in the semicontinuous polymerization. As it is mentioned before, the batch emulsion polymerization proceeds in three steps (nucleation, growth, depletion). If the nucleation step is long for any reason (low initiator concentration, low emulsifier conc., etc.), overlap between the nucleation and the growth stages can occur and that leads in most cases to a polydisperse latex. The situation in semicontinuous polymerization is more remarkable because the nucleation stage is extended throughout the course of polymerization. To overcome this drawback, the nucleation stage should be eliminated, which can be realized through the use of the so-called **seed polymerization**. Preformed latex with definite characteristics (particle size, particle size distribution, and solid content – generally below 20%) is used as a seed, which is able to capture free radical species from the aqueous phase as well as oligoradicals formed in the aqueous phase. So by the semicontinuous emulsion polymerization, a part of monomers (5-10%) is added at the beginning of polymerization and allows completing the conversion of those monomers (in-situ seed polymerization). The addition of the remaining monomers, either solely or as a pre-emulsion, provides for growth of the formed particles in the seed-stage. Semicontinuous polymerizations performed without use of a seed-stage more commonly suffer from change in the number of particle during the addition of the monomer [22-29]. If an emulsifier is introduced into the reactor during the addition step, the total emulsifier concentration in the aqueous phase shouldn’t exceed the critical micelle concentration in order to avoid the secondary nucleation. Furthermore, the type of semicontinuous process by means of monomer or pre-emulsion addition affects also significantly the particle size and particle size distribution. Firstly, the number of particles formed in the nucleation stage will be larger for the monomer addition than for the pre-emulsion addition process. Secondly, during the addition, two mechanisms are possible: 1) if the emulsifier present in the pre-emulsion leads to a secondary nucleation, the final particle size distribution will be very broad and the final particle number may be greater than for the latex produced by the monomer feed process. 2) if the secondary nucleation does not take place, the final particle number will be smaller than for latex prepared by monomer feed.

B) Control of the rate of polymerization

Wessling et al. [30] was the first one, who analyzed and determined the relationship between the rate of monomer addition (R_m) and the overall rate of polymerization (R_p) for a semicontinuous emulsion polymerization. Figure 1.2.2 displays the dependence of the overall polymerization rate on the addition rate for styrene semicontinuous emulsion polymerization at 70 °C [10].

The equation 6, which describes the rate of polymerization in correlation with the number of polymer particles, number of radicals per particle, and the monomer concentration within the polymer particles, can be rewritten as follows:

$$R_p = K[M]_p V_m \tag{10}$$

This is under the assumptions that, $\bar{n}$, $[M]_p$, and N_p are constant during the monomer addition and the polymerization occurs exclusively in monomer-swollen particles.

Where $$K = \frac{k_p \bar{n} N_p}{N_A V_m} \tag{11}$$

and V_m is the molar volume of the monomer. The product of $[M]_p V_m$ is the volume fraction, φ_m, of the monomer in the polymer particles. The rate of polymerization equation can be further simplified to

$$R_p = K\varphi_m \tag{12}$$

The accumulation of the monomer in the reaction vessel, which increases the volume of polymer particles, can be described as follows

$$\frac{dM}{dt} = R_m - R_p \tag{13}$$

The increase in the total particle volume (V) with the time is given by

$$\frac{dv}{dt} = V_m R_m - (V_m - V_p) R_p \tag{14}$$

where V_p is molar volume of the polymer. On the assumption that $[M]_p$ is constant during the monomer feeding, *dM/dt* and *dv/dt* can be simply related by

$$\frac{dM}{dt} = [R_p] \frac{dv}{dt} \tag{15}$$

Substituting equations 13 and 14 into eq. 15 and simplifying leads to the following equation

$$\frac{1}{R_p} = \frac{1}{K} + \frac{1}{R_m}\left(1 - [M]_p (V_m - V_p)\right) \tag{16}$$

For most systems, $\left([M]_p (V_m - V_p)\right)$ will take values in the range of 0.001-0.1, and the equation (16) can be reduced to the approximated form

$$\frac{1}{R_p} = \frac{1}{K} + \frac{1}{R_m} \tag{17}$$

By substituting K using equation 12, the last equation can be rearranged to give

$$R_p = R_m \varphi_p \tag{18}$$

where φ_p is the volume fraction of the polymer in monomer-swollen latex particles. In the most of semicontinuous emulsion polymerizations under starved feed conditions, φ_p > 0.8. Thus it is possible to control R_p through the choice of R_m. The above equation is only valid under the steady state condition when N_p, $[M]_p$, and $\bar{n}$ are constant. To reach the steady state, a finite time is required. It is worthily to note here, that some studies have shown that $\bar{n}$ increases with conversion and can take very high value (>> 100) during the semicontinuous polymerizations [31-32].

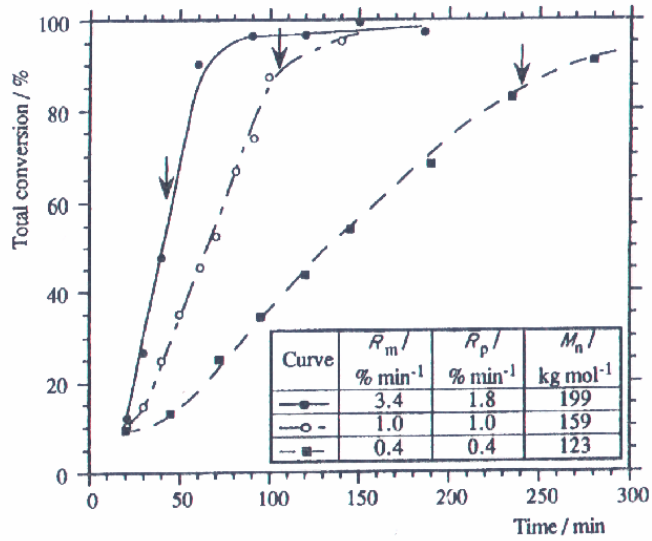

Figure 1.2.2. Dependence of the overall polymerization rate on the addition rate in semicontinuous emulsion polymerization of styrene at 70 °C [10].

C) Control of the heat of polymerization

Most of the free radical polymerizations are exothermic. The enthalpies of olefinic monomers are in the range of –60 to –100 kJ mol^{-1}. Typical rates of emulsion polymerization are of the order of 10^{-3} – 10^{-5} mol l^{-1} s^{-1}, which corresponds to approximate heat outputs in the range 0.6-100 J l^{-1} s^{-1}. Simple calculations show that the polymerization of 5 tons of vinyl acetate to give 50% solids of latex would result in approximate heat output of 500- 50000 kJ min^{-1} at typical rates of batch emulsion polymerization. This would lead to a temperature rise of around 200 °C if the reaction would be carried out under adiabatic conditions. From safety aspects, it is of great importance to use the semicontinuous process in order to achieve good heat removal through the addition of cold reactant and extend the polymerization and consequently the produced chemical

energy over a large period of time. Figure 1.2.3 shows the calorimetric diagram of a batch and analogous semicontinuous process for styrene polymerization [33]. The curve shows the extension of the rate and the heat of polymerization over the addition time.

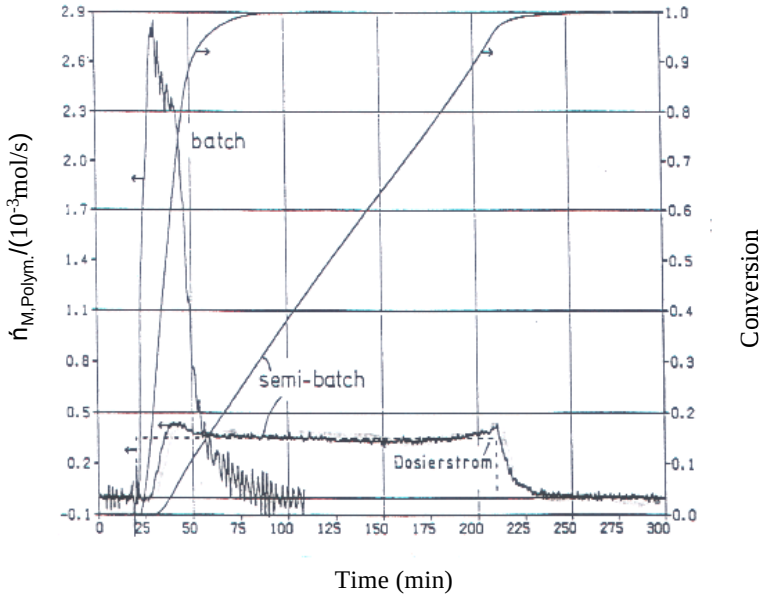

Figure 1.2.3. Evolution of the heat flow rate and conversion of styrene versus time [33].

D) Control of copolymer composition

The batch emulsion copolymerization of monomers exhibiting different reactivity ratios and/or water solubility produces copolymers with a drift of composition. For example, the batch copolymerization of vinyl acetate and butyl acrylate (VAc/BA) formed such a drift copolymer due to their different reactivity ratios. The reactivity ratios are r_{VAc} = 0.08, r_{BA} = 7.2 and their water solubilities at 20 °C are 0.291 and 0.006 mol/l, respectively. This indicates that BA polymerizes faster than VAc, which consequently leads to a copolymer rich in BA at the beginning of the reaction and at the end of polymerization the copolymers are richer in VAc. The copolymers are not really statistic, and therefore show two distinct glass transition temperatures representing the two monomer sequences in the copolymer. In contrast, the semicontinuous emulsion polymerization under monomer starved conditions, allows the formation of copolymers with homogeneous composition. Figure 1.2.4 shows the influence of the polymerization techniques on the physical properties (viscoelasticity) of the formed copolymers. Under starved conditions ($R_p \approx R_m$), the instantaneous conversion is usually over 80%. So the introduced monomers by semicontinuous processes polymerized rapidly and nearly completely upon entering the reactor. This leads to produce copolymers with an overall uniform composition.

Under these conditions, it was found that the copolymer composition during the course of the polymerization was similar to the initial monomer composition ratio. Furthermore, the copolymer shows only one T_g [17, 34, 35].

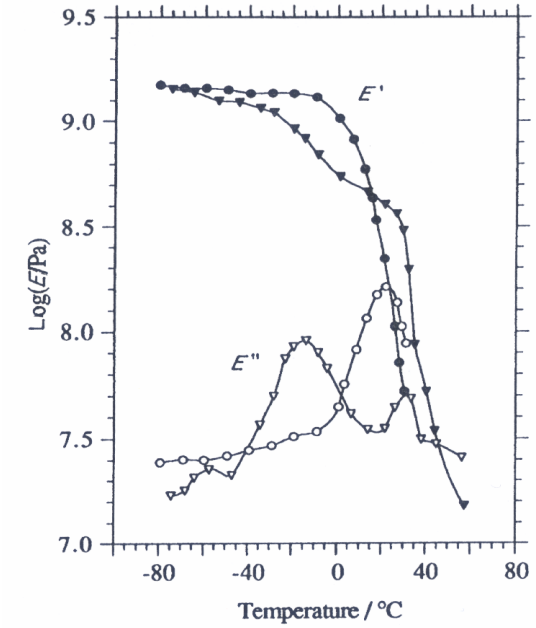

Figure 1.2.4. Dynamic mechanical spectra showing the variation of storage modulus (E') and loss modulus (E'') with temperature for copolymers prepared by emulsion copolymerization of vinyl acetate (71mol-%) with butyl acrylate (29 mol-%) using: (i) a batch process (▼, E'; Δ, E'') and (ii) a semicontinuous process operated under monomer starved condition (● , E'; ○, E'') [17].

E) Control of the molecular weight and molecular weight distribution

The average-molecular weight of polymers and their distributions play a key role in many applications. Under starved feed condition by semicontinuous emulsion polymerization, the monomer concentration in the polymer particle is very low. Hence the molar mass of the polymers formed is lower than the polymer produced under monomer flooded condition or batch polymerization for which $[M]_p$ has its maximum value, $[M]_p^{max}$. In the case of polymerization with low chain transfer and/or addition rates to already formed polymer, the molar mass of the produced polymer usually reduces with decreasing R_m. Chain transfer to polymer is important in the polymerization of some monomers such as VAc and most of acrylates, and it leads to the formation of long-chain branches. Additionally, crosslinking can occur if propagating branches terminate by combination. Such crosslinking occurs also under extremely low addition rate.

1.2.3.2. Other strategies for controlling copolymer composition

1. Controlled composition reactors

The main drawback of monomer starved addition is the low overall rate of polymerization and low productivity. Consequently, the molecular mass of the formed polymer may be low and the molecular weight distribution could be broader. Furthermore, undesired secondary nucleation

was also found [17]. Another strategy to control the copolymer composition in the case of flooded addition is the feeding of the individual monomers separately while monitoring the concentration of each monomer in the reactor on-line (e.g. by gas or liquid chromatography). The individual monomer feed rates are adjusted in such a way as to maintain the monomers composition in the reactor constant. Despite of the difficulties of this technique, tailor-made and uniform copolymer compositions were achieved [36-38].

2. Optimal monomer addition rate profile

This technique involves addition of the monomers at rates which vary with time in a manner calculated to maintain the copolymer composition constant during the course of polymerization [39-42]. For the calculation of the monomer addition profile some parameters such as the partitioning, reactivity ratios, and rate coefficients are required. Two strategies have been used:

1. Complete addition of the less reactive monomer to the reaction vessel at the beginning of the growth stage, followed by feeding of the more reactive monomer according to a calculated rate-time profile.
2. Independent addition of both monomers using a calculated rate-time profile.

It is not possible to predict the optimal addition profile directly but considerable experimental effort is required to support the calculations. This addition technique was investigated on VAc/MA and St/MA. In general the rate of polymerization with this technique is more rapidly than that by constant addition rate technique.

1.2.4. References

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1.3. Miniemulsion Polymerization

As described before, there are four different mechanisms for particle nucleation the so-called micellar, homogeneous, coagulative and monomer droplet nucleation. In the conventional emulsion polymerization, the monomer droplet nucleation is completely ruled out due to the low surface area of the monomer droplets (the ratio of monomer droplets to the number of micelles is about $1:10^8$). The only possible way to nucleate the monomer droplets is the preparation of stable monomer droplets with a diameter in the range of nanometer scale. In the last thirty years, many attempts were conducted to synthesize and polymerize stable monomer droplets. The term miniemulsion polymerization was used to describe the polymerization of monomer droplets with a particle size in the range of 50 to 500 nm. The preparation of miniemulsion can be simply achieved by subjecting an oil-water mixture to a very high shear. In recent years, many review articles have been reported by El-Aasser [1], Capek [2], Landfester [3] and Asua [4] on miniemulsion polymerization.

Back to the conventional emulsion, the emulsion systems are stabilized either electrostatically by using an ionic emulsifier such as sodium dodecyl sulfate (SDS), or sterically through non-ionic emulsifiers, such as alkyl polyethylene glycols, or block copolymers. This emulsion system normally suffers from the so-called Ostwald ripening process. This process refers to the diffusional degradation of small droplets, which have a high chemical potential, to larger one. Thus, emulsions subject to the Ostwald ripening effect are not stable and undergo phase separation upon standing for a short period of time. The Ostwald ripening process can be restrained by adding a costabilizer (a hydrophobic agent, ca. 1-10 wt-% based on the total amount of monomers). The costabilizers such as hexadecane and cetyl alcohol reduce the Gibbs free energy of the miniemulsion, thereby decreasing the driving force for the diffusion of the monomers into the aqueous phase.

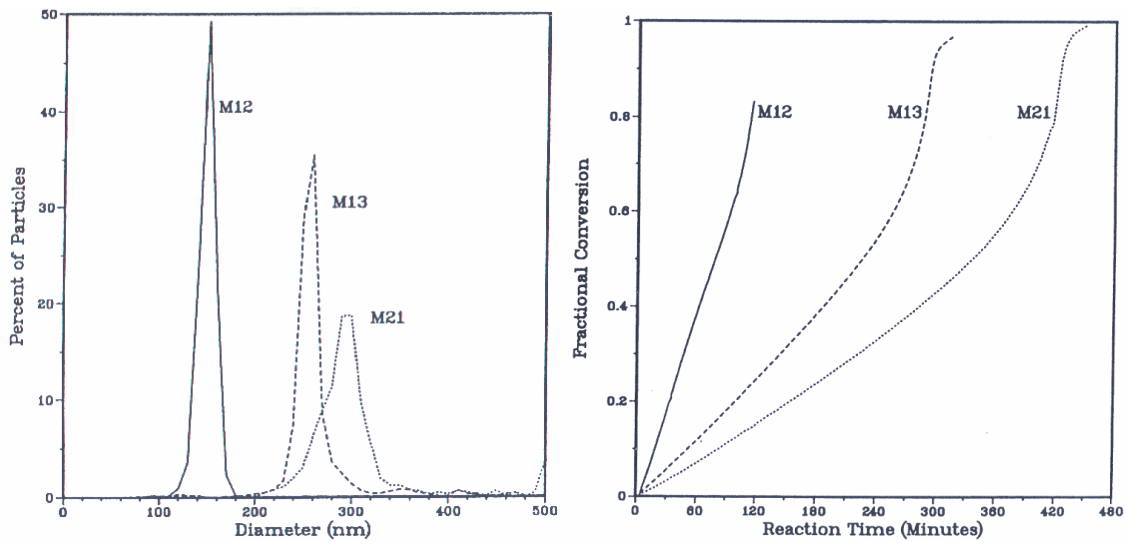
1.3.1. Components of miniemulsion

Most of the monomers polymerized via emulsion polymerization are suitable candidates for miniemulsion polymerization. It was reported on the miniemulsion polymerization of many monomers such as styrene [5-8], alkyl (meth)acrylate [9-12], VAc [13], vinyl chloride [14], vinyl hexanoate [15], and also on water-soluble monomers such as (meth)acrylic acid [16-18]. Various costabilizers were investigated, but cetyl alcohol and hexadecane are the most used costabilizers in many published papers [5-18]. After the polymerization, the costabilizer remains in the latex and it may have deleterious effects on the properties of the polymer. Alternatively, oil-soluble

initiators with long alkyl chain such as lauroyl and benzoyl peroxide, and 2,2´-azobisisobutyronitrile (AIBN) have been used as costabilizers [19, 20]. N-Dodecyl mercaptan was also used as costabilizer and chain transfer agent in the miniemulsion polymerization of MMA and St [11, 21]. Very hydrophobic monomers with a long carbon chain such as alkyl (meth)acrylates, i.e. dodecyl and stearyl methacrylate, were concurrently used as costabilizer and comonomer for St miniemulsion polymerization [22-24]. Hydrophobic or polar/hydrophobic polymers such as poly(St), poly(MMA) having a low molecular weight, were used also as costabilizer in the miniemulsion polymerization [7, 10]. Other hydrophobic additives such as dyes were also used as costabilizers [25].

Furthermore, together with the costabilizers, anionic [8], cationic [26], non-ionic emulsifiers [27] and mixed anionic/non-ionic surfactants [17, 18], as well as reactive surfactants have been used to stabilize the mini-droplets [28]. The main role of the surfactant here is to prevent the coalescence of the droplets.

In comparison to the classical emulsion polymerization, water-soluble initiators are also used to initiate the miniemulsion polymerization. Alternatively to these types of initiators, oil-soluble ones such as lauroyl and dibenzoyl peroxide, and AIBN can also be used [19, 20]. The polymerization in this case started and finished within the monomer droplets.



(a) (b)

Figure 1.3.1. Effect of the homogenization devices on the droplets size of miniemulsion (a) and on the conversion (b): M12 (prepared with the microfluidizer); M13 (sonifier); and M21 (omni mixer); all contained 5 mM SLS/20 mM HD and 20% styrene [29].

1.3.2. Methods of miniemulsion preparation

Generally, a miniemulsion system for polymerization consists of monomer(s), water, surfactant, costabilizer, and initiator. The monomer(s) and the costabilizer on the one side and the water, and the surfactant on the other side are stirred separately and then mixed together. This mixture is subjected to high efficient homogenization. The most important homogenization systems are rotor-stator, sonifier, and high pressure homogenizer. Rotor-stator systems and other shear systems (e.g. Ultra Turrax, Omni mixer) rely on turbulence to produce the emulsification. The sonifier produces ultrasonic waves leading the molecules to oscillate about their main position as the waves propagate. The shock waves produced on the total collapse of the bubbles cause break up of the surrounding monomer droplets. The region around the sonitrode is mostly affected by the waves, so it is important to keep the system under stirring for good homogenization. It was found for the sonication process that the particle size of the droplets is time dependent [29]. The microfluidizer and the Manton-Gaulin are the most commonly used high-pressure homogenizers. Coarse dispersions are pressurized using a positive displacement pump, and flow through a narrow gap at high velocity. A strong pressure drop occurs and the liquid leaves the valve gap as fine miniemulsion. High pressure homogenization produces miniemulsions with smaller size than ultrasonication, which in turn produces miniemulsions with smaller size than the rotor-stator homogenizer. Figure 1.3.1 shows the effect of the homogenizing technique on the droplets size as well as on the rate of polymerization. The homogenization process can be followed by different methods, e.g., turbidity and surface tension measurements.

1.3.3. Polymerization mechanisms and kinetic of miniemulsion

Most of miniemulsion polymerizations were carried out via free radical initiation. Water- or oil-soluble initiators were successfully used. The droplets nucleation suggests that the monomers inside the droplets polymerized directly via a radical capture that enters this monomer droplets and started the radical polymerization. The monomer droplets nucleation is the predominant nucleation mechanism for an ideal miniemulsion system. In some cases, depending on the reaction conditions, homogenous and micellar nucleation can not be absolutely ruled out. The ratio of the final number of particles to the initial number of monomer droplets ($N_{p,f}/N_{p,i}$) was used as gauge to estimate the nucleation mechanism in miniemulsion polymerization. When the value of this ratio is still around unity, droplets nucleation could be the dominant mechanism. This case was described by the term “one-to-one” copy, since the formed polymer particles are copy of the initial monomer droplets. That also means the droplets nucleation is the only nucleation mechanism. A low ratio indicates the incomplete droplets nucleation or coalescence

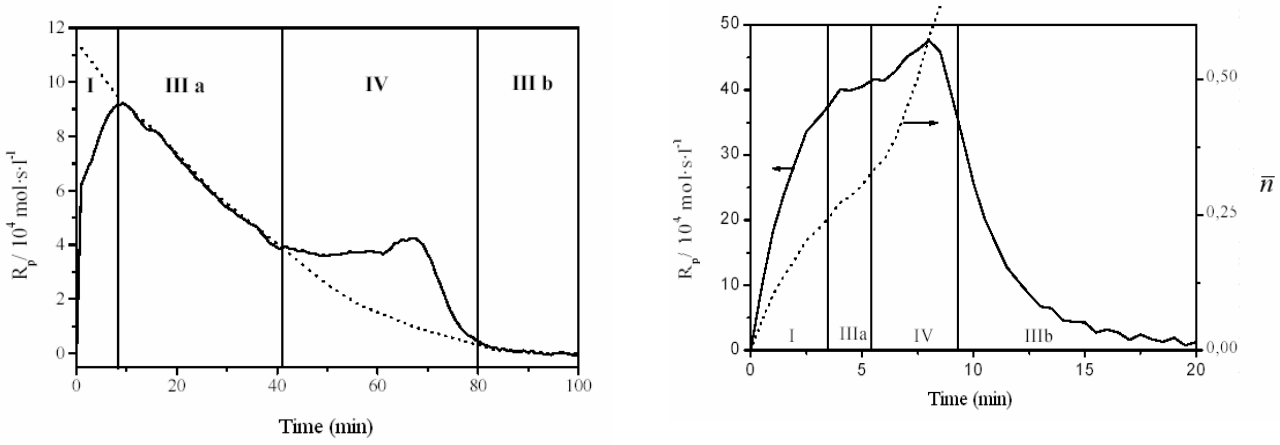
of the particles (coagulation). To the contrary, a higher value may be a signal for competition of other mechanisms such as micellar or homogeneous nucleation, due for example to the high surfactant concentration or to the high water solubility of the monomer. In most cases, micellar nucleation can be avoided by adjusting the surfactant concentration and the homogenization conditions to eliminate the free surfactant molecules from the system. The extent of the homogenous nucleation depends on some factors, which can be ordered as follow: The water solubility of the monomer(s), the concentration of the water soluble initiator, the type and concentration of the costabilizer. In the miniemulsion polymerization, the homogenous nucleation enhances usually with increasing water solubility of the monomer, initiator, and costabilizer. Generally, the stability of the droplets is an important factor in order to obtain fully droplets nucleation.

The kinetics of miniemulsion polymerization, as shown in Figure 1.3.2, can be divided into three intervals (I, III, IV):

- Interval I: nucleation interval
- Interval III a & III b : depletion interval
- Interval IV: gel effect

Similarly to microemulsion, there is no interval II, in which the rate of reaction is constant. Interval I is the nucleation interval, which ends when the number of radicals per particle reach the equilibrium state ($\bar{n} \approx 0.5$). During interval III, the kinetic follow s that of a bulk or suspension polymerization and the monomer is depleted exponentially. The average number of radical per particle is quite constant ($\bar{n} = 0.5$). Interval IV is related to the gel effect, which is due to the increase of the viscosity inside the polymer particles. This interval also is characterized by the increase of the number of radicals per particle ($\bar{n} > 0.5$). The gel peak appears obviously for miniemulsion system with a large particle size (d >100 nm).

It is of great importance to note the difference between the two calorimetric diagrams, which represents two different monomer types. In case of styrene (Figure 1.3.2 a), the gel effect is clearly observed in interval IV. In contrary, in the case of MMA (Figure 1.3.2 b), the polymerization is characterized by a self acceleration, the so-called Trommsdorf effect. In this case the gel effect (Interval IV) was detected after a short reaction time (5 min) and the number of radicals per particle increased dramatically versus time.



(a) (b)

Figure 1.3.2. Calorimetric investigation of R_p in miniemulsion polymerization of styrene by using KPS as initiator (a), and MMA by using an oil-soluble initiator (V59) (b) [30].

1.3.4. Effect of some parameters on the number of particles and the reaction rate

Generally, the decreasing of the droplets size leads to high droplet numbers and consequently high polymerization rates. The following parameters can significantly affect the droplets size and consequently the number of the polymerization loci and the rate of polymerization: the type and concentration of surfactant, the type and concentration of initiator, the type and concentration of costabilizer, the hydrophobic/hydrophilic nature of the monomer, and the monomer/water ratio. The investigation of such parameters was the scope of many publications in the last decade. It was found in many investigations on miniemulsions that anionic surfactants produced larger numbers of droplets, which lead usually to higher polymerization rates than the non-ionic surfactants. Furthermore, the number of droplets increases with the surfactant concentration, thereby increasing the rate of polymerization.

Another parameter is the initiator type, which can be soluble either in oil or water. In the case of an oil-soluble initiator, it is dissolved in a monomer with the costabilizer prior to the emulsification. In contrary, the water-soluble initiator is dissolved in water and added later to the miniemulsion just prior starting the polymerization. The effect of the water-soluble initiator on the miniemulsion polymerization kinetics is debatable and conflicting results have been reported. Theoretically, the initiator concentration shouldn't affect the number of droplets and consequently the rate of polymerization, if the polymerization proceeds under ideal miniemulsion conditions. Experimentally, it was found that the initiator concentration affects, in some cases, the number of droplets as well as the rate of polymerization. This effect is more pronounced at higher initiator concentration, high water solubility of the monomer(s) or insufficient amount of costabilizer. Oil-soluble initiators are suitable for monomers which show either high water solubility such as MMA and VAc or extremely low water solubility such as

lauryl methacrylate. Furthermore, oil-soluble initiators, especially these contain long alkyl chain such as lauryl peroxide (LPO), enhance the mini-droplets stability and act as costabilizers. The amount of the oil-soluble initiator has no effect on the droplets size but enhances the polymerization rate. The average molecular weight remains roughly constant at the beginning of the polymerization and then increases significantly at high conversion due to the gel effect. Generally, the decrease of the droplets size leads to high droplets numbers and consequently high polymerization rates.

1.3.5. Applications of miniemulsion polymerization

The main advantages of miniemulsion polymerization can be summarized as follows: Encapsulation of water-insoluble additives such as pigments, biological active substances and inorganic salts in the latex particles [31-34], production of latexes with high solid contents and low viscosities [6, 12, 17, 18, 35, 36], control of the monomer composition in the reaction loci (monomer droplets), implementation of anionic [37, 38] and step polymerization in aqueous dispersed media [39], incorporation of very hydrophobic monomers [22-25, 27, 40], and preparation of hybrid polymer particles [41-44]. A more interesting advantage of miniemulsion polymerization is the possibility of controlling the polymer molecular weight, its distribution, and the polymer composition through the living radical polymerization, e.g. stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT). The last application, RAFT in miniemulsion, will be the subject of chapter 5 in this work.

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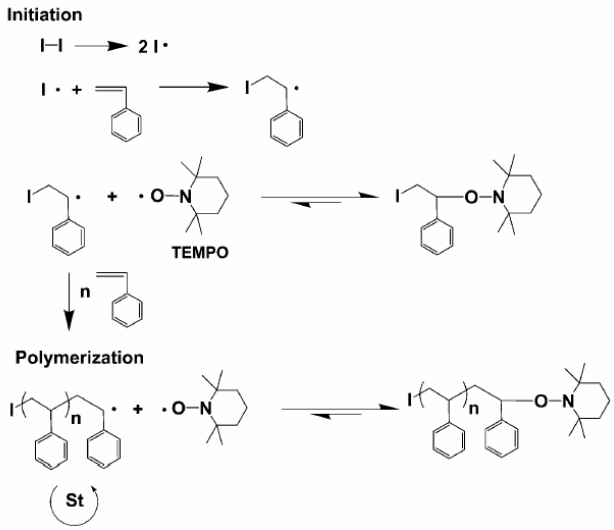
1.4. Living Radical Polymerization in Miniemulsion

Living/controlled radical polymerization has rapidly developed in the last 10 years [1-6]. This technique has opened the way to the synthesis of macromolecules with a desired macrostructure, architecture, and narrow molecular weight distribution. Living radical polymerization was intensively investigated in bulk and solution polymerization. The adaptation and optimization of the living radical polymerization to heterogeneous polymerizations such as suspension, emulsion and miniemulsion polymerization, will achieve a great commercial acceptance for new generation of polymer dispersions, produced by such techniques [7]. The main drawback of the living radical polymerization (LRP) in bulk and solution is the low rate of polymerization. Contrarily, the living free radical polymerization in heterogeneous systems (emulsion and miniemulsion) shows insignificant reaction-rate retardation. This could be related to the compartmentalization of free radicals in heterogeneous systems. Generally, this segregation prevents the termination reactions while preserving the overall concentration of the active chains.

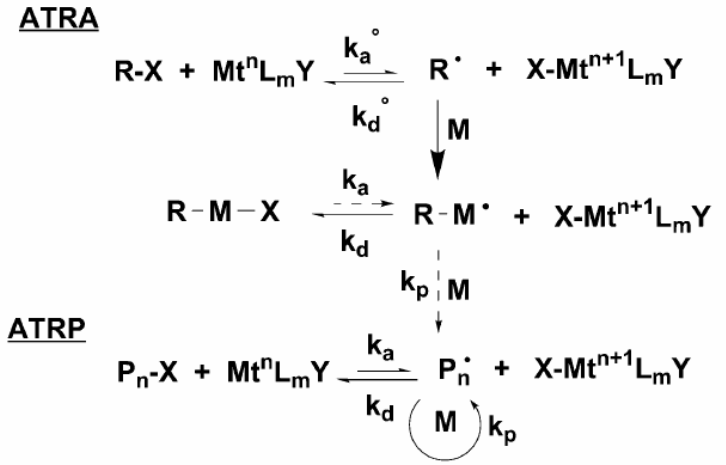


Scheme 1.4.1. Stable free radical polymerization (SFRP) by using a nitroxide agent.

Living free radical polymerizations are classified into two main groups according to the control of the chain growth: **reversible termination** or **reversible transfer**.

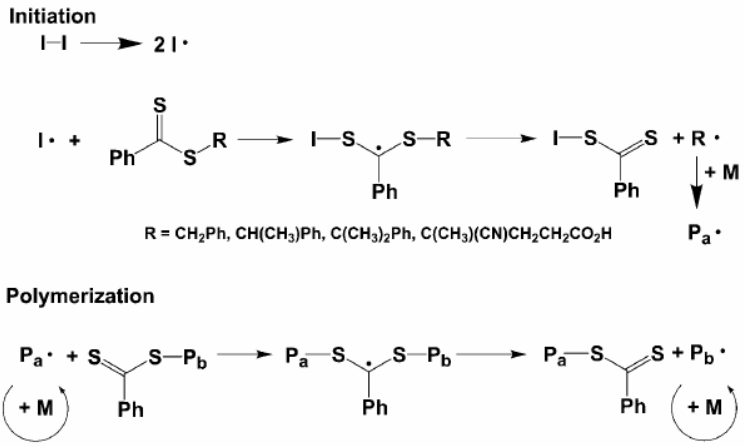
Reversible termination mechanisms, such as stable free radical polymerization (**SFRP**), i.e. nitroxide-mediated polymerization (Scheme 1.4.1), and atom transfer living radical polymerization (**ATRP**) (scheme 1.4.2), use a controlling agent that reacts reversibly with the propagating polymeric radical to yield a dormant polymeric chain. The equilibrium is strongly shifted towards the dormant species so that the active radical concentration is lower than in the conventional radical polymerization. The lowering of the radical concentration reduced

the rate of termination and preserves the living character of the chains. Important in the reversible termination mechanism is that all the chains are simultaneously initiated within a few minutes at the start of the reaction.



Scheme 1.4.2. Living radical polymerization by atom transfer mechanism (ATRP).

Reversible transfer mechanisms such as reversible addition-fragmentation transfer (**RAFT**) and degenerative transfer (DT) employ a chain transfer that reacts with propagating macroradicals. This type for controlling radical polymerizations is based on the chain transfer technique (scheme 1.4.3). In the case of reversible addition fragmentation chain transfer with dithioesters agents, the rate constant of chain transfer must be higher than the rate constant of propagation in order to get an effective control of the polymerization.



Scheme 1.4.3. Illustration of the concept of RAFT by using a conventional radical initiator.

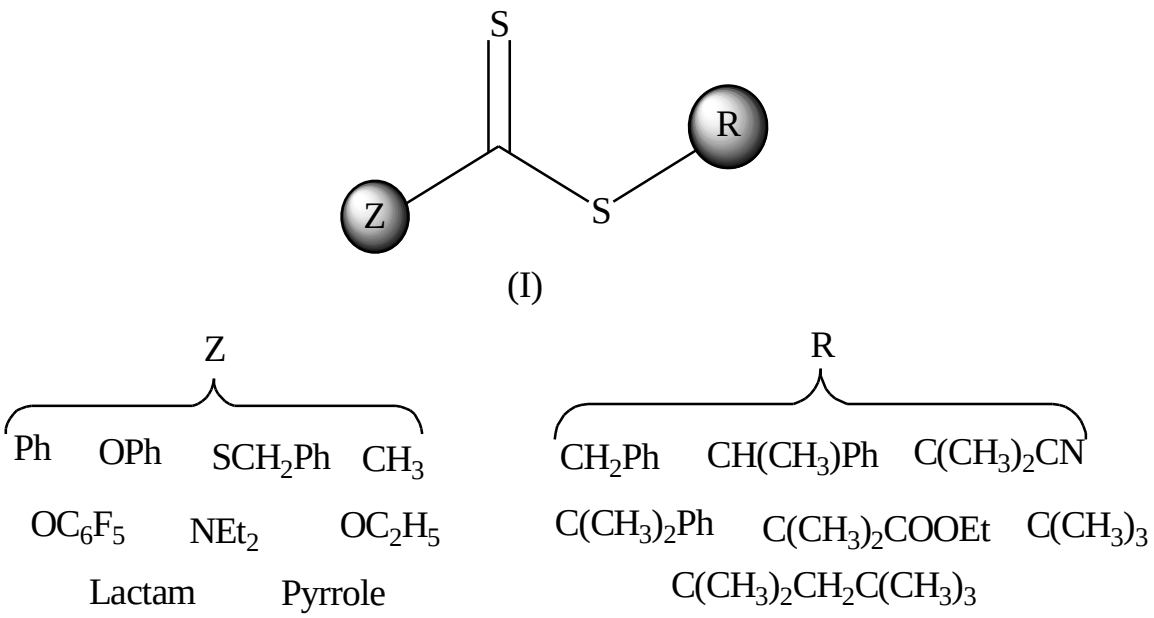
Ideally, the addition of a RAFT agent to a polymerization should not affect the polymerization rate. Actually it was found sometimes retardation in the polymerization rate especially in heterogeneous polymerization. In case of RAFT polymerization, a conventional initiator such as persulfate salts is used to initiate the polymerization. The chain transfer agent

is then consumed by the radical originated from the initiator decomposition. The total number of chains in the system is the sum of transfer agent and primary radical molecules.

1.4.1. Design and effectiveness of RAFT reagent

The more effective RAFT agents are certain thiocarbonylthio compounds (I) (Scheme 1.4.4), where Z is a group that modifies the reactivity of the thiocarbonyl group towards the free radical addition and R is a free radical leaving group [8, 9]. With appropriate choice of the RAFT agent and reaction conditions, the RAFT polymerization can be successfully used to produce polymers with a narrow polydispersity. The molecular weights are predetermined by the conversion and RAFT agent concentration. Moreover, the polymers obtained by the RAFT process can be chain extended or used as precursors for block copolymers synthesis by further addition of another monomer(s). The RAFT polymerization also provides a route to new polymeric materials with stars and more complex architectures. The RAFT agent will show good living character, if the following points are fulfilled:

1) a rapid exchange reactions
2) the chain transfer constant should be greater than 2
3) good homolytically leaving group, capable of reinitiation
4) constant number of chains during the polymerization



Scheme 1.4.4. Chemical structure of some thiocarbonylthio based RAFT agents.

1.4.2. Estimation of the transfer coefficient

The transfer constant or the transfer coefficient (C_{tr}), defined as the ratio of the transfer and propagation rate coefficients, is an important parameter in RAFT polymerization. In the case of reversible chain transfer, the rate of consumption of the transfer agent depends on the two transfer constants, C_{tr} (= k_{tr}/k_p) and C_{-tr} (= k_{-tr}/k_i).

$$\frac{d[RAFT]}{d[M]} \approx C_{tr} \frac{[RAFT]}{[M]+C_{tr}[RAFT]+C_{-tr}[D]} \quad (1)$$

If the rate of the reverse reaction between $R^{\bullet}$ and the polymeric RAFT agent (dormant species, *D*) is negligible, and the chain is long, then equation 1 can be simplified to Eq. 2;

$$\frac{d[RAFT]}{d[M]} \approx C_{tr} \frac{[RAFT]}{[M]} \quad (2)$$

$$C_{tr} = \frac{[M]d[RAFT]}{[RAFT]d[M]} = \frac{d(\ln[RAFT])}{d(\ln[M])} \quad (3)$$

The conversion of the RAFT agent can be calculated as follows.

$$\frac{d[RAFT]}{dt} = \frac{[RAFT]_0 - [RAFT]_t}{[RAFT]_0} = \left\{\frac{[M]_0 - [M]_t}{[RAFT]_0}\right\} \Big/ \left\{\frac{[M]_0 - [M]_t}{[RAFT]_0 - [RAFT]_t}\right\} = \frac{\overline{X}_n(calcd)}{\overline{X}_n(found)} \quad (4)$$

The transfer constants of various thiocarbonylthio compounds have been found to span more than five orders of magnitude (0.01 to >1000) depending on the groups of Z and R and the particular monomer(s) being polymerized. To yield narrow polydispersities below 1.5, the transfer constant of the RAFT agents should be greater than two.

$$\overline{M}_w / \overline{M}_n = 1 + \frac{1}{C_{tr}} \quad (5)$$

1.4.3. Calculation of the molecular weights

The number-average molecular weight in RAFT polymerization can be calculated with the following equation:

$$\overline{M}_n(calcd) = \frac{[M]_0 - [M]_t}{[RAFT]_0 + df([I]_0 - [I]_t)} m \quad (6)$$

where, $[M]_0$ is the initial monomer concentration in mol; $[M]_t$ the monomer concentration at time t in mol; *m*, the monomer molecular weight (g/mol); $[RAFT]_0$, the initial RAFT concentration in mol; $df([I]_0 - [I]_t)$, the number of initiator-derived chains produced *d*, the number of radical-radical reaction, and

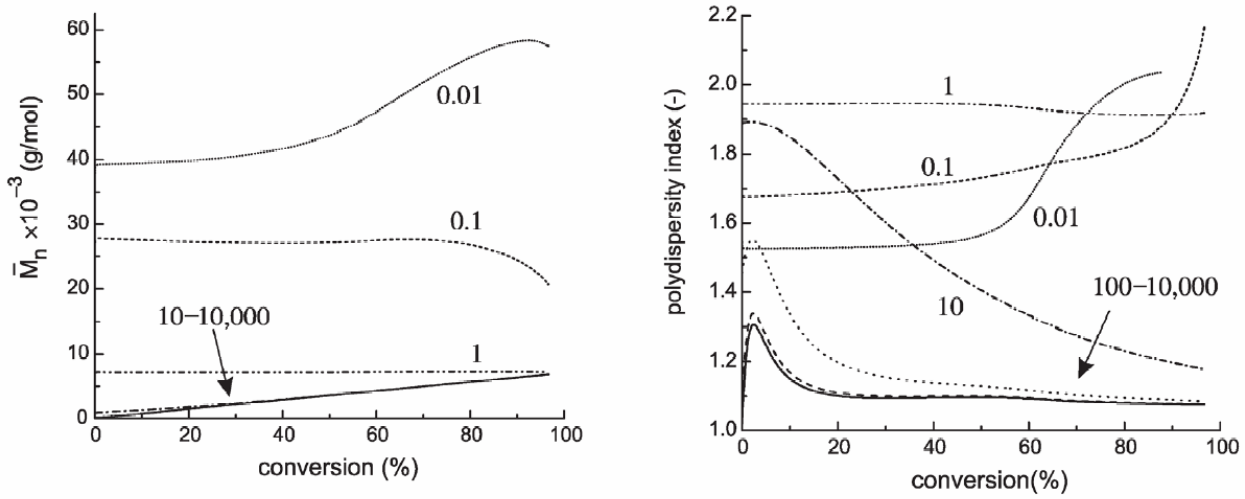
$$[I]_0 - [I]_t = [I]_0(1 - e^{-k_d t}) \quad (7)$$

where, k_d is the rate constant for initiator decomposition; *f*, the initiator efficiency. In many reactions with short reactions times or low initiator concentration, the term $df[I]_0(1-e^{-k_d t})$ is small with respect to $[RAFT]_0$ and can be neglected. Then equation 6 can be simplified to:

$$\overline{M}_n(calcd) = \frac{[\mathrm{M}]_0 \ \mathrm{X\ m}}{[RAFT]_0} \tag{8}$$

where X is the monomer conversion.

Figure 1.4.1 shows the estimated values for $\overline{M}_n$ and the polydispersity indexes (PI) at different C_{tr}.



(a) (b)

Figure 1.4.1. Simulation of the values of $\overline{M}_n$ and PI for styrene RAFT-polymerization in solution at 80 °C [styrene] = 3 mol/l, [AIBN] = 4.4 mol/l [10]. Different RAFT agents were used, which exhibit different C_{tr}-values.

1.4.4. RAFT in emulsion and miniemulsion polymerization

The use of RAFT in classical emulsion polymerization was first reported by Le et al. [6]. More recently, there have been a number of publications dealing with the use of RAFT in emulsion [11-18] and miniemulsion [19-22]. The main problem by the using of RAFT in batch emulsion polymerization is the diffusion of the RAFT agent through the water phase to the loci of polymerization and its distribution between the different phases (monomer droplets, polymer particles and aqueous phase). Avoiding the RAFT transport through the water phase by using the seed emulsion or miniemulsion polymerization has enhanced the living character of such systems.

To guarantee a well living polymerization in emulsion and miniemulsion, some basic requirements for RAFT agent should be fulfilled. Firstly, the RAFT agent has to be present in

the reaction loci (particles) since the beginning of the polymerization. Secondly, the transfer agent has to be homogeneously distributed among the particles, so that the same average molecular weight can be obtained in all particles. Thirdly, by the conventional emulsion polymerization, RAFT should be relatively water soluble to diffuse from the monomer droplets to the polymer particle in a time short enough compared to the duration of the polymerization. Finally, in the case of miniemulsion, the nucleation period should be very fast to achieve a good distribution to the RAFT agent between the polymer particles.

RAFT miniemulsion polymerization was conducted on styrene and some (meth)acrylate monomers such as butyl and methyl (meth)acrylate [21, 22]. The rate of polymerization by using RAFT agent was smaller than that of the conventional miniemulsion polymerization. It could be due to exit of the radicals formed by the first exchange of the RAFT agent from the polymer particles. In some investigations, it was observed that RAFT in miniemulsion of styrene stabilized by ionic emulsifier suffered from destabilization during the polymerization [21]. In contrary, with non-ionic emulsifier stable latex with low PI was obtained [22].

1.4.5. Living radical polymerization of monomers containing sugar moieties

Recently, few vinyl sugar monomers were polymerized by using controlled living polymerization techniques [23]. Ohno et al. polymerized for the first time a styrene carrying saccharide monomer by nitroxide-mediated polymerization (NMP) [24, 25]. The polymerization of isopropylidene-glucose carrying acrylate (AIpGlc) was conducted also by NMP [26]. The synthesis of the block copolymer poly(St-b-AIpGlc) was also achieved. Four isopropylidene-sugars carrying styrene were polymerized in bulk at 130 °C by NMP [27, 28]. Block copolymers with styrene were also prepared and the deprotected polymers exhibited amphiphilic character. 4-vinylbenzyl glucoside peracetate was polymerized in chlorobenzene at 125 °C by using TEMPO affording a polymer with low polydispersity (1.1) [29]. Fukuda et al. reported on the polymerization of 3-MDG by ATRP with an alkyl halide/copper complex system in veratrole (1,2-Dimethoxybenzene) at 80 °C [30]. Controlled molecular weight up to M_n = 20x10^4 g/mol and low polydispersity, $1.2 \leq M_w/M_n \leq 1.5$ w ere obtained. Poly(St-b-3-MDG) block copolymer with narrow molecular weight has been synthesized by the sequential addition technique. A 3-MDG graft copolymer has also been synthesized [31]. Chen and Wulff have used the ATRP technique to produce ABA and star amphiphilic block copolymer of poly(methacrylate) bearing a galactose fragment and poly (ε-caprolactone) [32]. Narain and Armes have reported on the polymerization of 2-glucoamidoethyl methacrylate (GAMA) and

2-lactobinoamidoethyl methacrylate (LAMA) using ATRP [33, 34]. Block copolymers of GAMA and LAMA with other monomers were also synthesized.

1.4.6. References

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Chapter 2

Semicontinuous emulsion copolymerization of 3-MDG/BA by monomer feed addition

2.1 ABSTRACT:

New polymer colloids based on saccharide monomer, using of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG), were prepared by semicontinuous emulsion polymerization, a widely used industrial process. The copolymerization of 3-MDG and BA, by the monomer addition technique, at 70°C, using sodium persulfate ($Na_2S_2O_8$) as an initiator, was investigated. The influence of some reaction parameters, such as the type and concentration of the surfactants as well as the monomer addition rate (R_m) on the polymerization rate (R_p), the colloidal properties, and the stability of the latexes, was studied. It was found that under starved-feed conditions the polymerization rate and the particle size (D) increased with an increasing rate of monomer addition. The weight-average molecular weight ($\overline{M}_w$) also increased by enhancing R_m and a narrower molecular weight distribution was obtained. Furthermore, the type and the concentration of surfactants strongly influenced the particles size and its distribution. The effect of the seed-stage on the particle size and its distribution was also investigated.

2.2 INTRODUCTION

Semicontinuous emulsion copolymerization by monomer feed technique involves the metering of neat monomer(s) and initiator, separately, to the reaction vessel containing water, surfactant, buffer and usually a "pre-charge", which may be consists of a part of initiator and a part of monomer(s). The monosaccharide derivative 3-MDG has been investigated in batch emulsion homo- and copolymerization yielding the so-called "sugar latexes" with interesting properties [35-37 in chapter 1.1]. Table 2.1 shows the most physical parameters of 3-MDG and BA. The two monomers (3-MDG and BA) exhibit different reactivity ratios, which led to the formation of copolymers with relatively heterogeneous macrostructure. The higher reactivity of 3-MDG means a more consumption than BA at the beginning of the reaction, and at the end of polymerization the copolymer is richer in BA.

Table 2.1. Some important parameters of 3-MDG and BA

Parameter	3-MDG	BA
state	white crystal	liquid
water solubility (g/l)	2.44	2.20
density (g/ml)	1.19	0.89
T_g (°C)	167	-54
k_p [a)] (L/mol . s)	1265	2400
reactivity ratio	1.94	0.54
Q-value	0.56	0.38
e-value	0.20	0.85

[a] The value at 70 °C.

So, to avoid this composition drift, it is important to control the monomer composition in the reaction loci, i.e. in polymer particles. On the other hand, the sparingly water solubility of 3-MDG and BA are comparable, which means that the monomers distribution between the different phases will be relatively the same. Furthermore, we have used the monomer feed technique under starved feed condition in order to maintain the monomer concentration within the polymer particles as low as possible to control the rate of polymerization. Semicontinuous

emulsion polymerization under flooded conditions with the optimal additions profile was not used in this work.

We will discuss briefly the main features of the monomer feed technique.

- Under starved condition, the rate of polymerization (R_p) depends mainly on the monomer addition rate (R_m) and the system takes a significant time to reach the steady state, wherein the rate of polymerization is equal to the rate of addition. The time needed to reach the steady state depends on the number of particles, water solubility and diffusion rate of monomers, the monomer feed rate, and the level and type of surfactant. Increasing R_m extends the time required to reach the steady state. Briefly, by using this technique, the nucleation phase will be extended comparatively to the conventional emulsion polymerization.
- The addition of the total amount of surfactant at the outset of polymerization without monomer addition in the pre-charge leads to the formation of higher number of particles (N_p) than the batch process. Furthermore, the particle size (D), under normal polymerization conditions ([surfactant]>CMC), is in the range of 50 nm and the end latex is in most cases polydisperse. The most probable nucleation mechanism here is the micellar nucleation and the nucleation interval is extended over the entire duration of polymerization. There is instability in number of particles over the course of polymerization and secondary coagulation could be observed.
- The addition of a part of surfactant at the beginning of polymerization and the rest during the polymerization gives sometimes higher particle size than batch polymerization. Micellar and homogeneous nucleation mechanisms could simultaneously occur.
- The time of growth for an individual particle must be considered. The particles formed early in the reaction medium have a longer growth period compared to those later formed during the polymerization. When the period of particle formation is extended, this would tend to have a broadening effect on the particle size distribution.
- Industrially, the semicontinuous emulsion polymerization is usually conducted with a pre-charge to control the particles number. This takes place by addition of about 5-10% of the monomer(s) at the beginning of the reaction and allows completing conversion. In this case, the formed or nucleated particles could be considered as seed latex. This seed stage separates the nucleation from the growth step, and the addition of the rest of monomer provides the growth of the seed particles. This avoids also a secondary nucleation and lowers the particle size distribution of the end latexes.

In this study, the influence of some reaction parameters such as the type and concentration of the surfactants as well as the monomer addition rate on the kinetic features, the chemical, thermal and colloidal properties and the stability of the latexes was studied. A part of this study was finally devoted to investigate the effect of the state of the particles, formed in the early stage of emulsion polymerization, on the particles growth as well as on the particles number and size distribution.

2.3 EXPERMENTAL

2.3.1 Materials

3-MDG was prepared in our laboratory as described in literature (see appendix 1, p. 153). BA (Fluka) was distilled under reduced pressure just before use. All the other materials were used as received. Sodium persulfate $Na_2S_2O_8$ (Fluka) and sodium hydrogen carbonate $NaHCO_3$ (Merck) were used as an initiator and buffer, respectively. The following ionic surfactants, sodium lauryl sulfate (SDS, Merck), sodium lauryl ether sulfate (SLES, Henkel), sodium nonyl phenyl polyethylene glycol ether sulfate (NOS10, Wittco) and the nonionic surfactant nonyl phenyl polyglycol (HV25, Wittco), were used.

Table 2.2. Recipe of the semicontinuous emulsion polymerization of 3-MDG/BA at 70°C.

	Charge (g)	Feed I (g)	Feed II (g)
Water	102	-	18
$NaHCO_3$	0.12	-	-
Surfactant	variable	-	-
$Na_2S_2O_8$	0.012	-	0.110
3-MDG	-	17.30	-
BA	-	12.60	-

2.3.2 Polymerization Procedure

Semicontinuous emulsion polymerization was carried out at 70°C according to the recipe in Table 2.2. The monomer ratio of 3-MDG/BA (35/65 mol %) was used in most of the polymerizations in this work, which formed copolymers with a glass transition temperature of ~ 45°C. The polymerization was carried out in a 250-ml double-wall glass reactor equipped with a glass paddle-type stirrer, a reflux condenser, nitrogen inlet, and temperature sensor. Two titrating pumps, (Perfusor, type 100, from KD Scientific Inc.) and (Perfusor® compact, B|Braun Melsungen AG), were used to feed the monomer mixture and the initiator solution. First, the reactor was charged under a nitrogen atmosphere by deionized, degassed water, the surfactant and the buffer. The reaction medium was maintained under constant agitation of 175 rpm at 70°C for 30 min, followed by the addition of 10% of the total amount of the

initiator. Directly, the polymerization was started by feeding the reactor. The feed was divided into two streams. The first one was a mixture of both monomers in the required ratio, and the second was a solution of initiator. The flow rates of these streams were 0.16 and 0.1 g/min, respectively, and were kept constant during the polymerization. Nevertheless, for studying the effect of the monomer-addition rate, the addition time and, consequently, the rate of monomer addition were varied. The rate of monomer addition was low enough to ensure monomer-starved conditions in the reactor. The addition time was 3 h and the polymerization was continued in batch for further 30 min. To follow the reaction, at least 10 samples were withdrawn from the reactor during the polymerization. The reactions of the samples were stopped with hydrochinon and they were kept for some minutes in an ice bath.

2.3.4 Characterization of the Latexes

2.3.4.1 Monomer Conversion

The conversion was determined gravimetrically as well as by gas chromatography (GC). For total conversion by the gravimetric method, about 0.5 g of latex sample was weighted in a glass watch and dried under vacuum for at least 4 h at 50°C. The individual monomer conversion was followed by GC. The apparatus consists of a GC 14-B unit, hydrogen flame ionization detector (FID), auto sampler AOC-17 and capillary column. The capillary column, with a length of 50 m, 0.32-mm inner diameter, and a layer thickness of 0.5 µm, was filled with Crossbond, 95%-dimethyl, 5%-diphenyl polysiloxane, as a stationary phase. The measurements were carried out by two-step heating program. Nitrogen was used as a carrier gas with a pressure of 100 kPa. The hydrogen and air pressure were 60 kPa and 50 kPa, respectively (see appendix 9, p. 165). For the preparation of the samples, about 1 ml latex was diluted with 1 ml methanol to precipitate the polymer, which had been separated by centrifugation (15,000 rpm), and then toluene, as an internal standard, was added to the solution. Figure 2.1 shows a typical GC-chromatogram of the polymerization system, in the presence of toluene as an internal standard, indicating the retention times of the different components.

2.3.4.2 Calculation of the conversion

Two conversions were calculated: an instantaneous conversion and a total conversion. Instantaneous conversion was defined as the ratio of the polymer present in the reactor to the monomer fed into the reactor at that time. The total conversion was defined as the ratio of the

polymer present in the reactor to the total monomer used in the recipe (see appendix 8, p. 164). The amounts of samples withdrawn were taken into consideration for the calculation of the overall and instantaneous conversions.

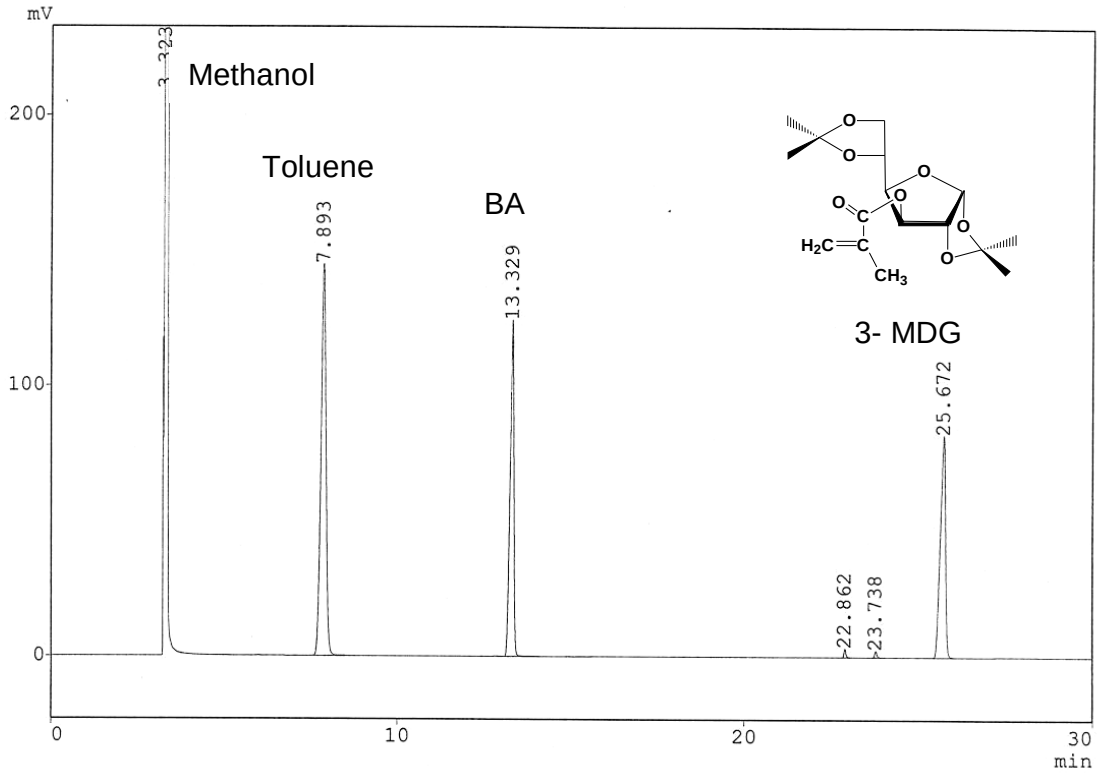


Figure 2.1. GC-chromatogram of 3-MDG/BA in presence of toluene as internal standard. The heating rates of the two steps were 15°C/min. The oven and the column temperatures were 210 and 240, respectively.

2.3.4.3 Particle Size and Particle Size Distribution

These were measured by quasi-elastic light-scattering method (Zetasizer 3, from Malvern Instruments, Ltd.). One or two droplets of the latex samples were diluted with about 20 ml of 1 mmol NaCl solution. The total number of particles (N_p) in milliliters latex was calculated by the following equation (2.1):

$$N_p = 6 \times 10^{21}\ TS_t / \pi\, D^3\, \rho \qquad (2.1)$$

where TS_t is the solid content at time (t) in 1 g latex; ρ, the density of the polymer; and, D is the average particle size (nm).

The particle size by QELS was calculated by using the Stokes-Einstein equation (Eq. 2.2). The diffusion coefficient, d, is determined by Eq. 2.3:

$$D = \frac{K_B T}{3\pi\eta d} \qquad (2.2)$$

$$C(\tau) = A\ exp(-2d\ K^2\tau)+B \qquad (2.3)$$

where, D is the particle size; K_B, Boltzmann´s constant; T, absolute temperature; d, diffusion coefficient; η, the viscosity of the medium; $C(\tau)$ the autocorrelation function; τ, delay time, A, B, and K constants.

The polydispersity index (*PDI*) was determined from the light scattering measurements using the cumulants technique. In the cumulant method, the correlation function g(τ) is analyzed by fitting a second order polynomial (in τ) to the logarithm of the measured function after removal of the baseline, over a span of τ determined by the channel selection and the setting of the correlator, i.e.:

$$\text{Log}\ \{(G(\tau)/ \langle N \rangle^2 - 1) = L+M\ \tau +N\ \tau^2 \qquad (2.4)$$

where, L, M, and N are constants which are fit by the cumulants analysis. The particle size distribution or the polydispersity index was defined as $Q = N/(2M^2)$. Q is close to the variance (width) of the size distribution. The cumulant method cannot determine the real shape of the size distribution, but simply measures its mean and polydispersity. It was supposed that the value of 0.04 is the boundary between mono- and polydisperse particles.

Transmission electron microscopy (TEM; Philips 300) allows the estimation of the particle sizes and their distributions in the dried state. For the preparation of the samples to be observed, the latexes were highly diluted in an aqueous solution of phosphotungstic acid (1%) as negative staining and mounted on copper grids, which were coated with carbon. The grids were dried at room temperature and then examined.

2.3.4.4 Electrophoresis

Experiments were performed with a Zeta Ziser 3 (from Malvern Instruments, Ldt.) at 25°C. The electrophoretic mobilities (μ) were measured at constant ionic strength (10^{-3} M NaCl). The measurements were performed three times and were readily reproducible. The electrokinetic potentials, or more frequently, the zeta-potentials (ζ) were calculated using either Hückel's (2.5) or Smoluchowski's equation (2.6), depending on the distortion of the applied field by particle and double layer:

for $KR \ll 1$ $$\mu = \frac{v}{E} = \frac{2\varepsilon_r \varepsilon_o \zeta}{3\eta} \qquad (\mu m\ s^{-1}/V\ cm^{-1}) \qquad (2.5)$$

for $KR \gg 1$ $$\mu = \frac{v}{E} = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} \qquad (\mu m\ s^{-1}/V\ cm^{-1}) \qquad (2.6)$$

where v is the particle velocity; E, the electrical field; ε_o, the permittivity of the free space, ε_r the relative permittivity of the medium, η, the viscosity of the medium; K^{-1}, the Debye thickness of the diffuse part of the double layer; and R, the radius of a spherical particle.

2.3.4.5 Copolymer Composition

The copolymer compositions were determined from ^{1}H NMR spectra, carried out on a Bruker AM 400 spectrometer. The measurements were performed at room temperature on a polymer solution in $CDCl_3$ (about 0.06 g/ml), containing tetramethylsilane (TMS) as internal standard.

2.3.4.6 Molecular Weights

The weight-average molecular weights ($\overline{M}_w$) were determined by gel permeation chromatography (GPC) on-line with a multi-angle laser light scattering (MALLS) and a refractive index detector. The polymers were dissolved in chloroform (3g/l) and the analyses were performed at 25°C using a GRAM-3000 (10 μm, 300 x 7.5 mm^2) column, filled with polyester gel (from PSS Polymer Standards Service GmbH). Chloroform was used as an eluent with a flow rate of 1 ml/min. The refractive index increment, *dn/dc*, of 3-MDG/BA copolymer was measured on a light-scattering photometer at 25°C in chloroform, and at a wave length of 633 nm. The *dn/dc* of the copolymer (3-MDG/BA; 35/65 mol %) was found to be 0.042 ml/g.

2.4 RESULTS AND DISCUSSION

2.4.1 Effect of the Monomer Addition Rate

In the batch process, the rate of polymerization (R_p) depends on the number of particles (N_p), which depends mainly on the initiator (I) and surfactant (S) concentrations [1]:

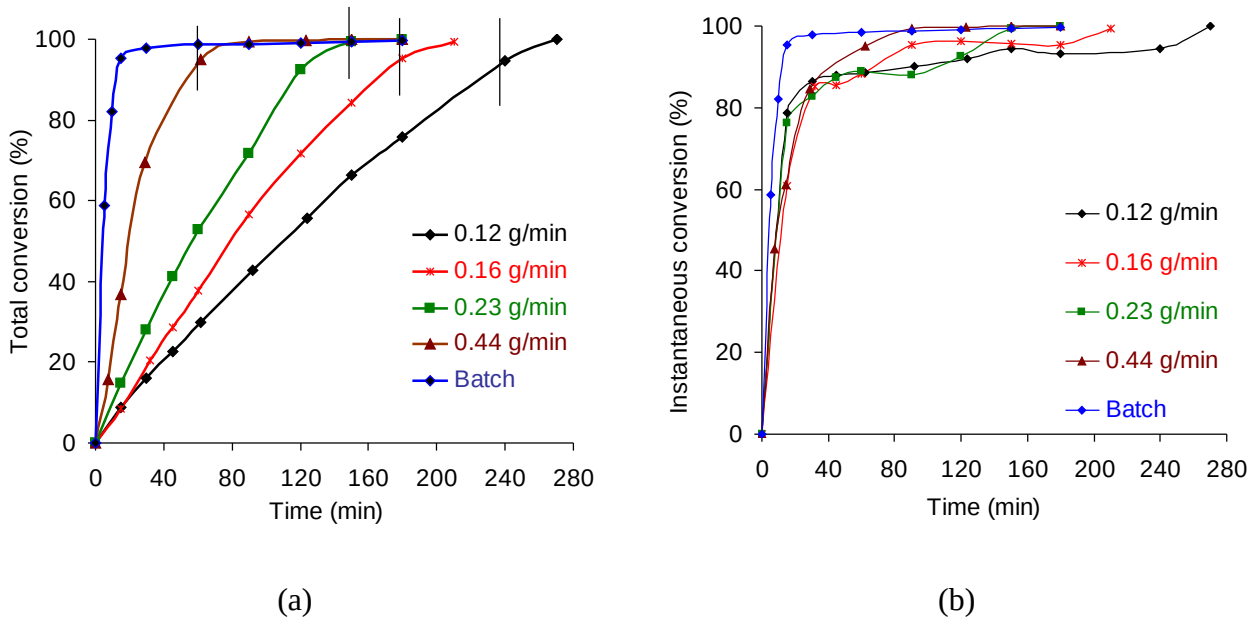
$$R_p \propto N_p \propto [I]^{2/5} [S]^{3/5} \quad (2.7)$$

In the semicontinuous process, the polymerization rate depends predominately on the addition rate of the monomer. If the monomer-addition rate (R_m) is high enough to maintain the saturation value of the monomer concentration within the latex particles $[M]_p$, the rate of polymerization (R_p) will be independent of the addition rate (flooded region) and consequently equation 2.7 is applicable in this case. Furthermore, if the monomer-addition rate is low enough, to ensure that the $[M]_p$ is below the saturation value, the polymerization rate approaches a constant value, which, therefore, depends only on the monomer-addition rate (controlled region). In that case, equation 2.7 is not applicable.

Table 2.3. Effect of the monomer-addition rate in semicontinuous process (versus batch process) on the final particle sizes and their distributions as well as on the average molecular weights of the end polymers and their polydispersities ($\overline{M}_w/\overline{M}_n$).

	Batch process	Semicontinuous process			
$R_m \times 10^5$ (g/min)	-	0.44	0.23	0.16	0.12
$R_m \times 10^5$ (mol/s)	-	3.70	1.93	1.33	1.01
$R_p \times 10^5$ (mol/s)	10.23	3.66	1.90	1.31	0.98
D (nm)	72	58.3	52.0	49.5	46.6
$N_p \times 10^{-15}$ (cm^{-3})	1.07	2.03	2.85	3.30	4.08
PDI	0.05	0.068	0.086	0.084	0.068
$\overline{M}_n \times 10^3$ (g/mol)	825	275	153	73	42
$\overline{M}_w \times 10^3$ (g/mol)	1221	429	272	133	86
$\overline{M}_z \times 10^3$ (g/mol)	1810	773	526	308	197
$\overline{M}_w/\overline{M}_n$	1.48	1.56	1.78	1.82	2.05

Four experiments were carried out with different monomer-addition rates, to study the effect of the monomer-addition rate on the polymerization rate, on the colloidal properties (particle sizes and their distributions), as well as on the average molecular weights and their distributions. SDS was used as an anionic surfactant, above its critical micelle concentration (CMC) value, with a concentration of 5 g/l, and all other additives were used as described in Table 2.2. The same amount and composition of the initial monomer mixture (3-MDG/BA; 35/65 mol %) were used, but the addition time was varied as described in Table 2.3. Batch polymerization was carried out with the same formulation as in Table 2.2, to compare the results with the semicontinuous one.



(a) (b)

Figure 2.2. Conversion-time curves of batch and semicontinuous emulsion copolymerization of 3-MDG/BA at different rates of monomer addition, according to recipe described in Table 2.2: (a) total conversion (the cross lines indicate the end of feeding); and (b) instantaneous conversion.

As shown in Figure 2.2 (a), the overall polymerization rate in batch process is very high (10.23×10^{-5} mol/s), due to the high reactivity of the sugar monomer. More than 95% total conversion was reached after only 15 min. In semicontinuous reactions, R_p directly depends on R_m. The rate of polymerization was calculated experimentally from the slopes of the nominally linear regions of the total conversion. As can be seen from Table 2.3, the monomer-addition rate (R_m) and the calculated reaction rate (R_p) are relatively the same, which confirmed that all the reactions were carried out under starved-feed condition. Figure 2.2 (b) shows the evolution of instantaneous conversion versus time. After about

10 min from starting the polymerization, all the instantaneous conversions reached the maximum value (more than 90%).

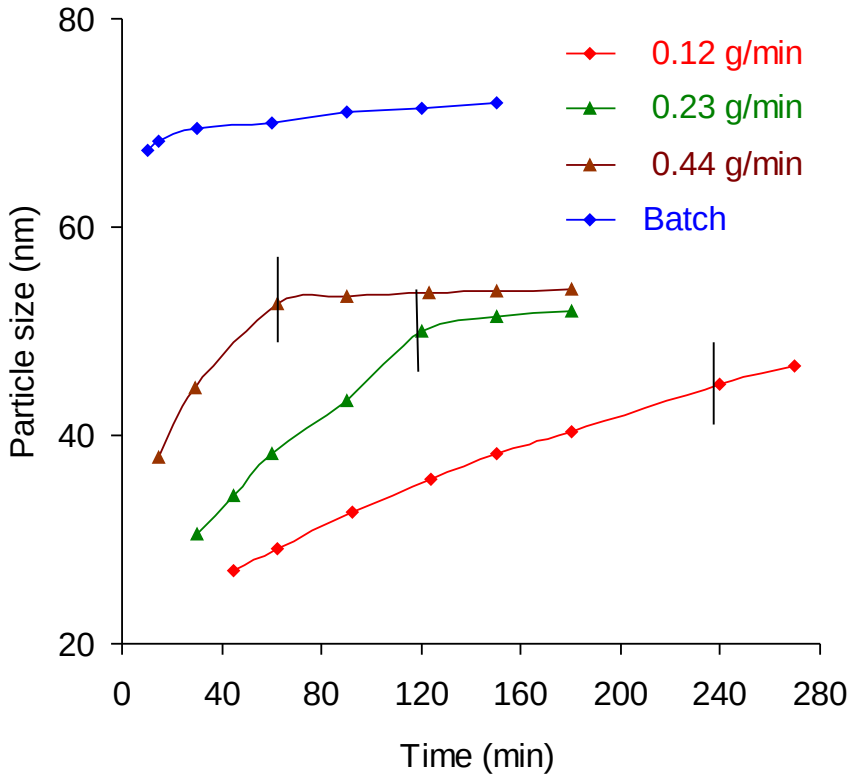


Figure 2.3. Particle-size evolution against time for semicontinuous copolymerization of 3-MDG/BA at different monomer-addition rates, according to Table 2.3. The cross lines indicate the end of feeding.

The effect of the addition rate on the evolution of particle size (D) and the number of particles (N_p) during the polymerization is shown in Figures 2.3 and 2.4. It was found that, if the addition rate increases, the particle size also increases and, therefore, the number of particles decreases. In the case of the batch process, the particle size reached, after a short time, its maximum value and remained constant. In the case of the semicontinuous process, the particle sizes increased slowly and continually until the end of the monomer addition. As shown in Table 2.3, a final particle size of 72 nm was obtained in batch, whereas in the semicontinuous process, the final sizes were smaller and they increased from 46 to 58 nm with increasing of R_m from 0.12 to 0.44 g/min. Nevertheless, the PDI of the batch latex is narrower than those formed by semicontinuous polymerization using the monomer-addition technique. Moreover, it was found that, under our experimental conditions, the rate of monomer addition has no remarkable influence on the particle-size distribution and the final latexes are polydisperse. As shown in Figure 2.4, the total number of particles decreases with

increasing the monomer-addition rates. Sajjadi [2] derived a correlation for particle formation under monomer-starved conditions for hydrophobic monomers such as styrene and found that N_p is inversely proportional to the 0.66th order of R_m. In this work, the proportionality factor was -0.50. Moreover, it can be seen from the curves that, above 45% conversion, the number of particles decreases continuously until the end of polymerization, which indicates a secondary coagulation. This behavior increased with lowering of the monomer-addition rates. It may be due to the low monomer concentration in the polymer particles and to the huge number of very small particles, which were formed at the beginning of the reaction, and stabilized through coagulation.

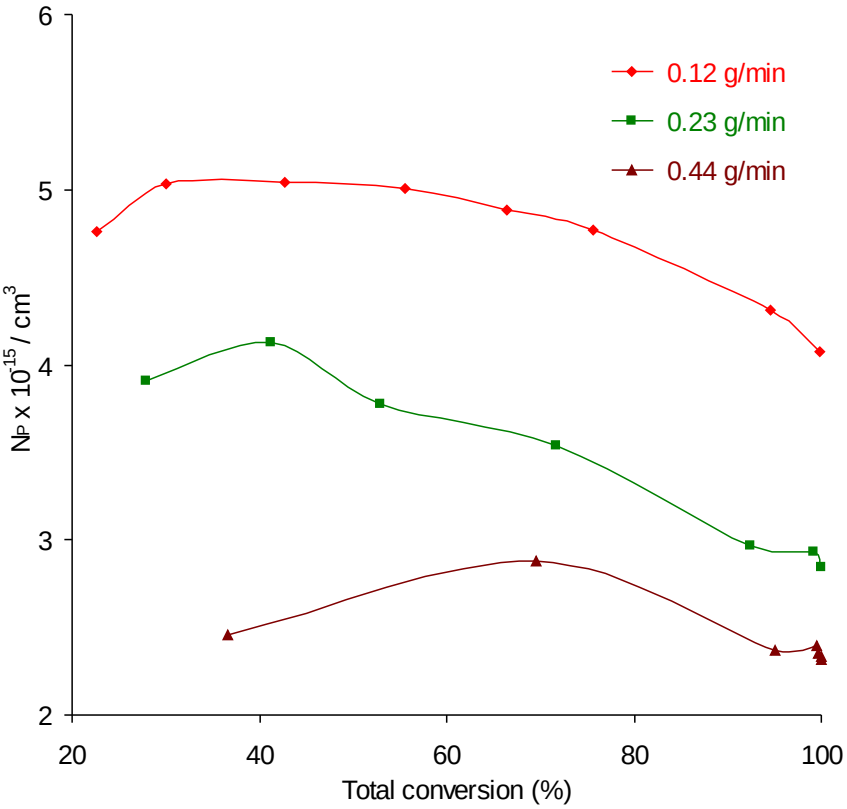


Figure 2.4. Total number of particles (N_p) against the total conversion for semicontinuous polymerization of 3-MDG/BA at different monomer addition rate, according to Table 2.3.

The rate of monomer addition affected not only the colloidal properties (*D*, *PDI*), but also the properties of polymer, such as the average molecular weight. By using the semicontinuous process, it is possible to control the weight-average molecular weight ($\overline{M}_w$) and the molecular weight distribution (MWD), characterized by the polydispersity index (*PI*) and defined as the ratio of $\overline{M}_w/\overline{M}_n$. The copolymer formed by the batch process exhibits higher weight-average molecular weight than that of those formed by the semicontinuous process, as

shown in Table 2.3. This could be related to the maximum saturation value of $[M]_p$ in the batch process. Under starved-feed conditions, $\overline{M}_w$ depends on the monomer-addition rate. As the addition rate increases, $[M]_p$ increases, which leads to the increase of the $\overline{M}_w$ value. The decrease of $\overline{M}_w$ is due mainly to the lowering of the monomer concentration within the polymer particles and/or to the increase of the chain transfers reactions to polymer. A bimodal distribution has been obtained in the case of VAc/BA copolymerization [3], due to the chain transfer to monomer and polymer. In our system, all the GPC-analyses of the sugar copolymers exhibited a monomodal distribution. The low PIs indicate, rather, that the termination reactions occurred through a combination at high R_m and through disproportionation at low R_m.

2.4.2 Effect of the Surfactant Concentration

One of the most important parameters in emulsion polymerization is the surfactant. The main role of surfactant is stabilizing the monomer droplets in an emulsion form, decreasing the surface tension in the reaction medium and stabilizing the formed latex particles. The CMC is a specific parameter for each surfactant, which controls the particle-formation mechanism. According to the HUFT-theory [4], the particle formation undergoes “homogeneous nucleation”, if the surfactant concentration is below the CMC. Polymerization under this mechanism will form particles with a more uniform size (monodisperse). If the surfactant concentration is above the CMC, the particle formation undergoes “micellar nucleation”, in which the monomer-swollen micelles are the major loci of particle nucleation. Oligoradicals generated in the aqueous phase enter into these micelles, and form particle nuclei. Polymerization proceeds from the monomer supplied by the monomer droplets by diffusion through the aqueous phase.

To study the effect of the surfactant concentration on the reaction pathway as well as on the colloidal properties, four semicontinuous emulsion polymerizations, using surfactant concentrations below and above the CMC, were carried out. We used SDS, which has the CMC of 2.8 g/l, as an anionic surfactant with concentrations of 1, 3, 5, and 10 g/l. The initial monomer composition of 3-MDG/BA was 35/65 in mol and the amount of SDS was added at the outset of the reaction (in the charge). All the reactions were carried out under starved-feed conditions, where the addition rate was 0.16 g/min.

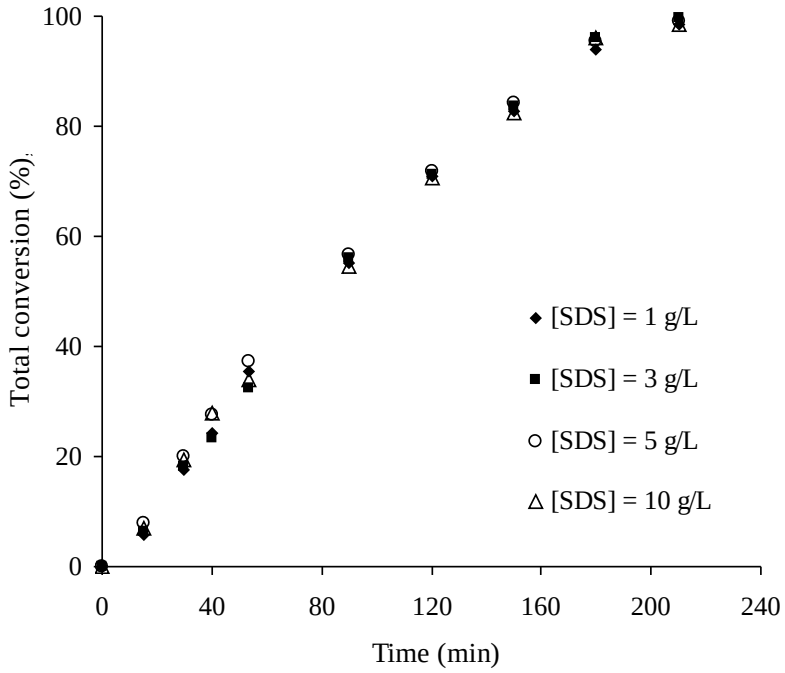


Figure 2.5. Conversion-time curves of semicontinuous copolymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.

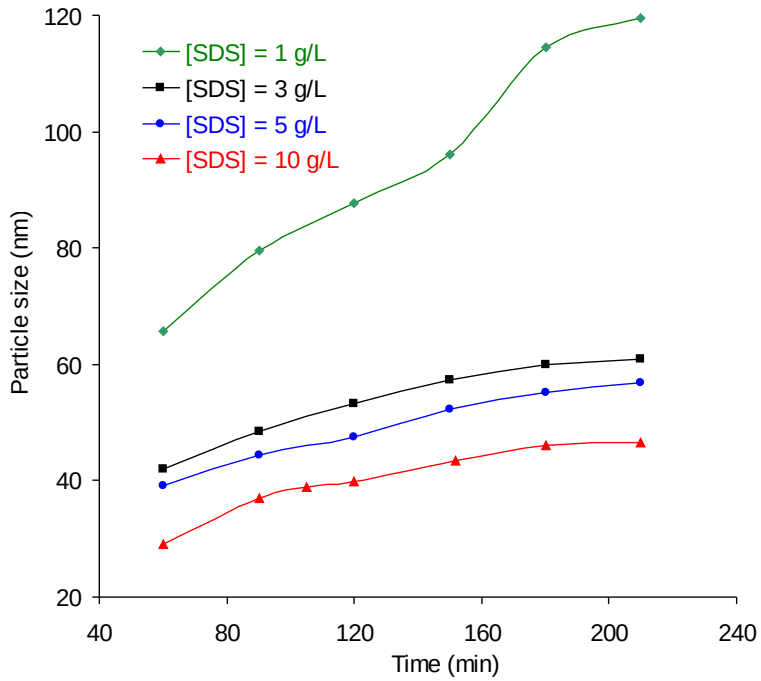


Figure 2.6. Particle size evolution against time for semicontinuous emulsion copolymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.

It was found that the rate of the polymerization is independent of the surfactant concentration (Figure 2.5). This behavior is completely different from the case of the batch process, in

which the polymerization rate as well as the number of particles is generally proportionally to the 0.6^{th} power of the surfactant concentration.

In the semicontinuous process, the surfactant concentration influences the particle size evolution and the particle-size distribution. As shown in Figure 2.6, if the surfactant concentration is above the CMC, the surfactant concentration has a little effect on the particle size. The high concentration of the surfactant at the outset of the polymerization leads to form a huge number of free micelles, which are able to capture and stabilize the formed oligoradicals in the aqueous phase. If the surfactant concentration is below the CMC, homogeneous nucleation takes place. The primary particles are then stabilized through coagulation by means of Brownian motion, which continued until the resulting polymer particles had enough surface ionic groups, leading to their stabilizations by mutual repulsion forces. The resulting final particles size is bigger than the former one by a factor of 3.

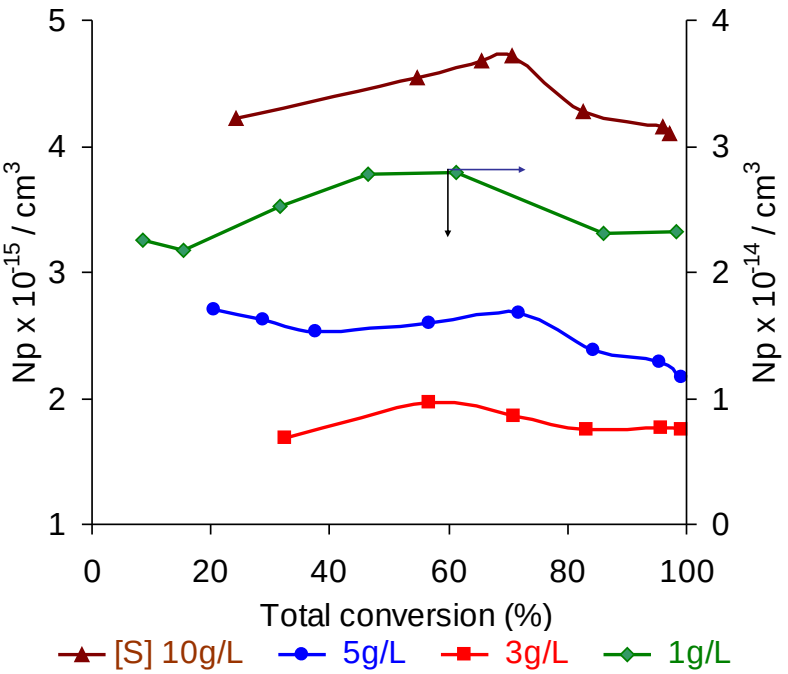
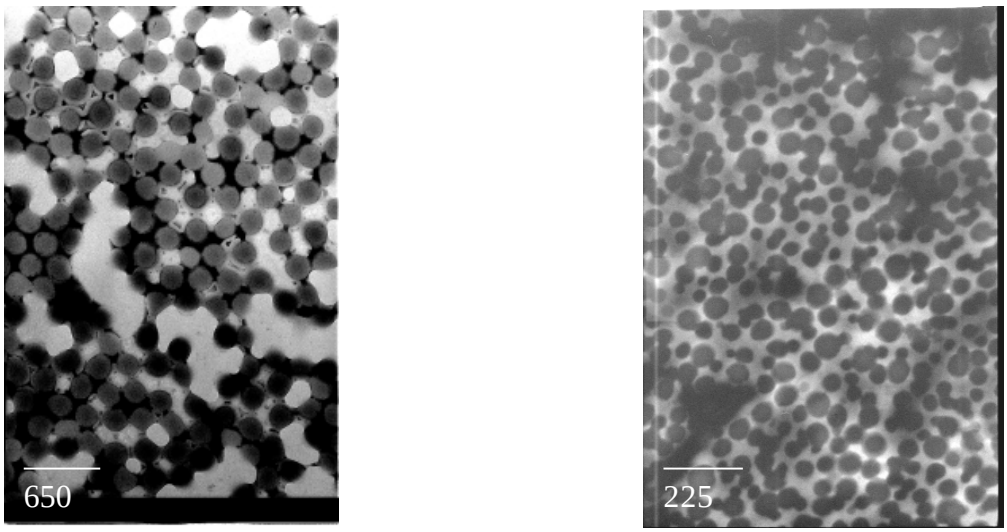


Figure 2.7. Total number of particles (N_p) against the total conversion curves of semicontinuous polymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.

In the semicontinuous processes, particles are formed over the entire duration of the polymerization process [5], so that the surfactant concentration influences the particle numbers evolution during the polymerization. Figure 2.7 shows the evolution of N_p versus the total conversion. The curves can be divided into three regions. The first one is until about 40% conversion and shows an increase of the number of particles. The second one, from 40 to

about 70% conversion, shows a stability of the number of particles. The last region, above 70% conversion, shows a decrease in the number of particles, which could be related to a secondary coagulation. This coagulation is relatively high, if the surfactant concentration is below the CMC-value. It was also found that, the particle-size distribution is clearly affected by the surfactant concentration. Below the CMC, a PDI of 0.04 was obtained, which is smaller than those founded above the CMC (PDI = 0.125). We can assume that the increase of the surfactant concentration leads to a broader particle-size distribution**.** This is due to the ability of the surfactant to stabilize the newly formed particles in the last period of the reaction. The TEM micrographs of two sugar latexes prepared with different surfactant concentrations show that, below the CMC (Figure 2.8, a), the particles are nearly monodisperse (PDI = 0.04) and, above the CMC (Figure 2.8, b), the particles are polydisperse (PDI = 0.125).



(a) (b)

Figure 2.8. TEM Micrographs of two sugar latexes formed at two surfactant concentrations; (a) [SDS] < CMC (1 cm = 630 nm); and (b) [SDS] > CMC (1 cm = 225 nm).

The relationship between the surfactant concentration and the final particle size as well as the final number of particles is illustrated in Figure 2.9. We can see that N_p increases and, simultaneously, the particle size (D) decreases, with an increasing SDS concentration. The curve of N_p is characteristic for monomers, which have low water solubility. Interestingly, N_p increases more rapidly with SDS concentration above the CMC, due to the higher solubility of both hydrophobic monomers in the surfactant micelles, in which more favorable interactions with the hydrocarbon core of the micelles take places.

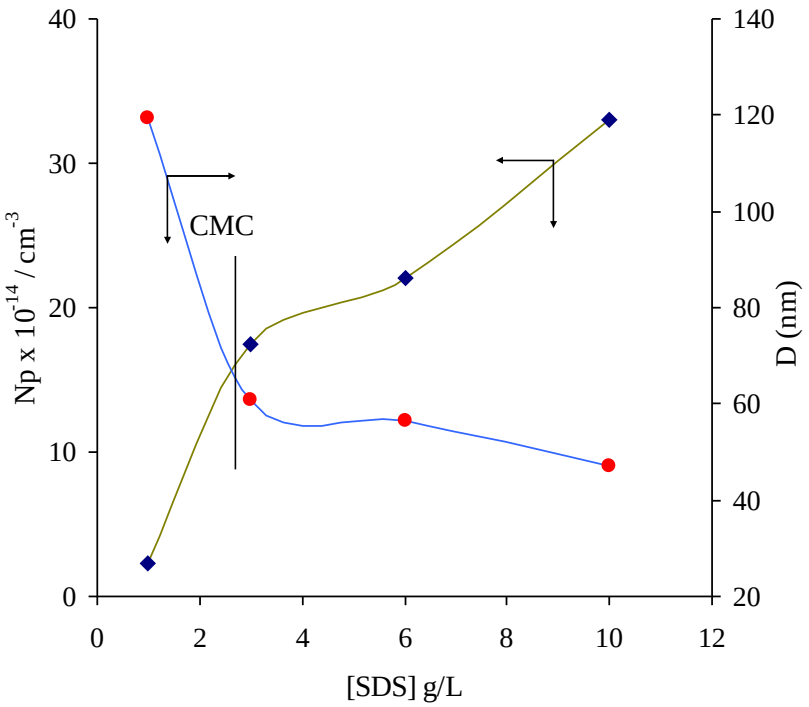


Figure 2.9. Relationship among [SDS], *D* and N_p of the final latexes.

2.4.3 Effect of the Type of the Surfactant

The type of surfactant has a great influence on the stability and the size of particles. SDS, SLES and NOS10 as anionic surfactants, with different chemical structures and molecular weights, as well as HV25 as a nonionic surfactant, were used to investigate their effect on the particle size of the sugar latexes. The polymerizations were carried out at the same surfactant concentration (5 g/l) and under starved condition with a monomer-addition rate of 0.16 g/min. It was found that, the type of surfactant did not influence the reaction rate (Figure 2.10). The instantaneous conversions reached a maximal value (more than 90%) after 15 min and remained constant. In all cases, a maximum total conversion, more than 99%, was obtained at the end of the reaction. Figure 2.11 shows the evolution of the particle size throughout the polymerization. By using SDS and SLES, the final particle sizes were relatively the same. NOS10 led to a larger particle size than in the cases of SDS and SLES. The larger particle size was obtained by using of HV25. Similar behavior has been found by Unzueta and Forcada in the case of seeded semicontinuous emulsion copolymerization of MMA/BA, using SDS and two nonionic surfactants, such as Brij35 (ICI) and Glytanox1001 (Glyco Iberia) [6]. By using anionic surfactants, the numbers of particles are relatively stable during the reaction (Figure 2.12).

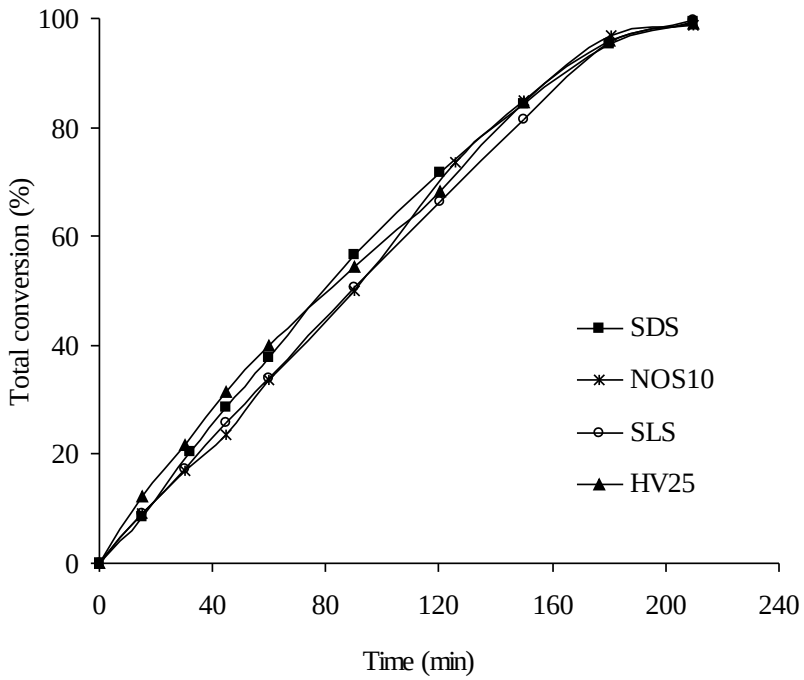


Figure 2.10. Total conversion-time curves of semicontinuous emulsion copolymerization of 3-MDG/BA with different surfactants, according to recipe described in Table 2.2.

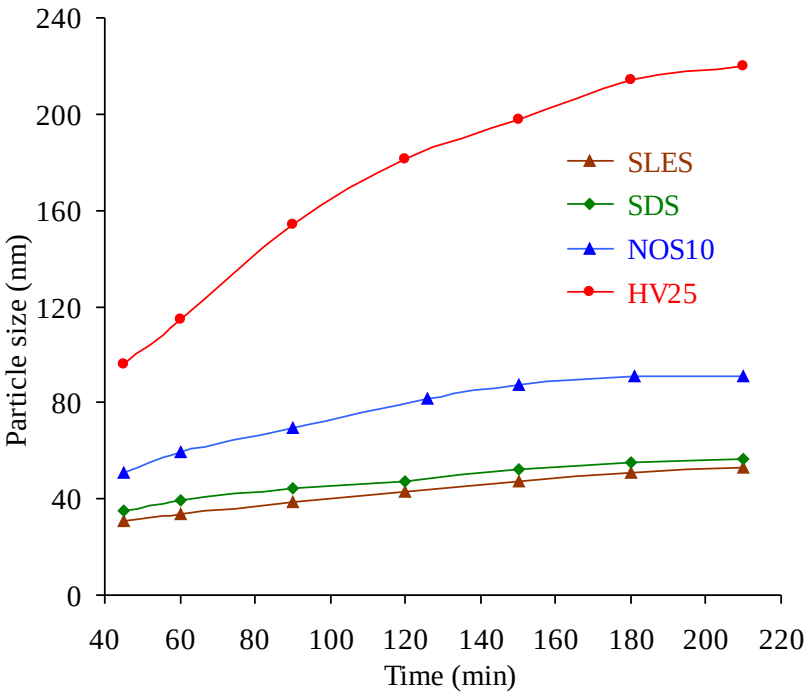


Figure 2.11. Particle size-time curves of semicontinuous copolymerization of 3-MDG/BA. The concentration of the surfactants SDS, SLES, NOS10 and HV25 was 5g/l, and all other constituents were maintained as described in Table 2.2.

But in the case of HV25, in which the polymer particles are stabilized sterically, the number of particles decreased drastically until about 50-60% overall conversion, and then remained

relatively stable. To understand this behavior, let us first give an example for using HV25 as a nonionic surfactant in the batch emulsion copolymerization of MMA and BA [7]. It was found that the emulsion copolymerization of MMA/BA follows the classical theory of the micellar nucleation. In comparison to SDS emulsion copolymerization, a higher polymerization rate, shorter nucleation stage and complete conversion were obtained by using HV25 at a concentration of 5 g/l. Furthermore, by increasing the initiator concentration, N_p decreases during the steady state period (phase II), which characterizes a polymerizing system, where the large number of particles, nucleated within a very short duration, are not stabilized enough by the nonionic surfactant to counteract the increase in the ionic strength. It is also conceivable that this high number of original particles may cause the burial of more HV25 surfactant inside themselves.

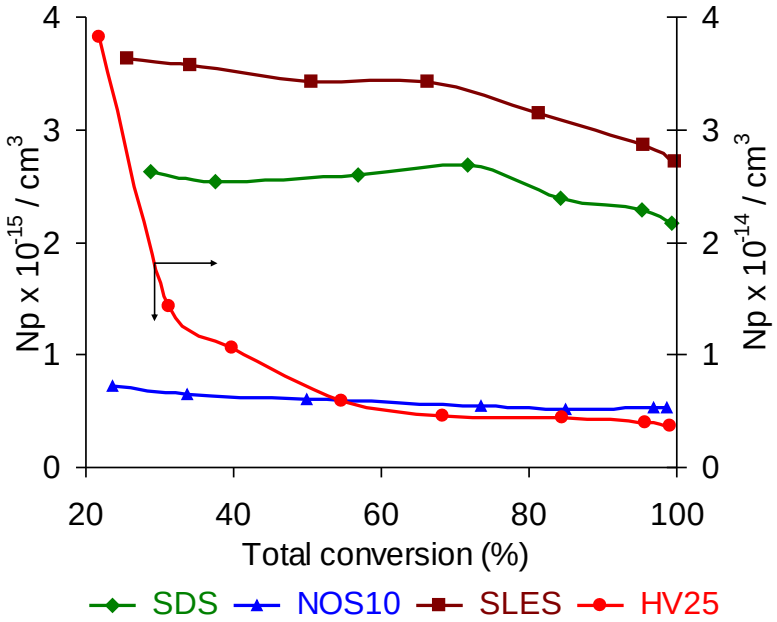


Figure 2.12. N_p, against the total conversion for semicontinuous emulsion copolymerization of 3-MDG/BA. The concentration of the surfactants SDS, SLES, NOS10 and HV25 was 5g/l, and all other constituents were maintained as described in Table 2.2.

In this work, similar behaviors were found: In the semicontinuous process, the monomer-addition technique, the surfactant/monomer ratio at the beginning the reaction is very high, which leads to production of a huge number of particles. During the polymerization, the monomer (polymer)/surfactant ratio increases and then the surfactant is not able to stabilize all of this number of particles, especially when using a nonionic surfactant, which may be buried inside the particles. So, this massive decrease in the particle numbers can be related to

the coagulation mechanism, by which the charge on the outer surface increased until it reached a state in which the surface charges were able to stabilize the particles. This sharp decrease in the number of particles was also mentioned by Fitch and Tsai [8] for the emulsion polymerization of MMA at low surfactant concentration and in the total absence of a surfactant. It was suggested that this decrease can only happen by the aggregation of particles by coagulation, in which two charged particles undergo a Brownian collision, stick together and fuse. As the coagulation progresses and as more oligoradicals are adsorbed, the surface charge density of the resulting particles increases, which, in turn, increases their surface electrical potential, leading to a greater mutual repulsion and reduction in the overall average rate of coagulation. In our case, it seems that the concentration of HV25 used was not high enough to ensure a complete steric stability of the polymer particles, so that coagulation took place and the number of particles decreased tremendously. As the polymerization progressed, the polymer particle surface was more and more charged, arising from the initiator-derived polymer end groups, which contribute to stabilize the particles ionically as well as sterically. As shown in Figure 2.13, the zeta potential of the particles stabilized with HV25 increases with an increasing the total conversion. The increase in zeta potential was not linear with the conversion. At the beginning of the polymerization, the evolution of the zeta potential was low until 50% of total conversion, then increased obviously to –38 mV at 85%, and, finally, slowly increased to – 43 mV at about 99% of total conversion, which is enough to stabilize the polymer particles.

The average number of radicals per latex particle, which gives an indication of the reaction mechanism, was calculated according to the following equation (2.8):

$$\bar{n} = R_p N_A / k_p [M]_p N_p \qquad (2.8)$$

where $\bar{n}$ is the average number of radicals per latex particle, R_p, the rate of polymerization (mol L^{-1} s^{-1}); k_p, the overall propagation reaction constant (L mol^{-1} s^{-1}); N_A, Avogadro´s constant (mol^{-1}); $[M]_p$, the molar concentration of the monomer in the latex particles; and N_p, the total number of the particles per unit volume of the emulsion (L^{-1}). R_p and $[M]_p$ were determined experimentally and k_p was estimated as described in the literature [9].

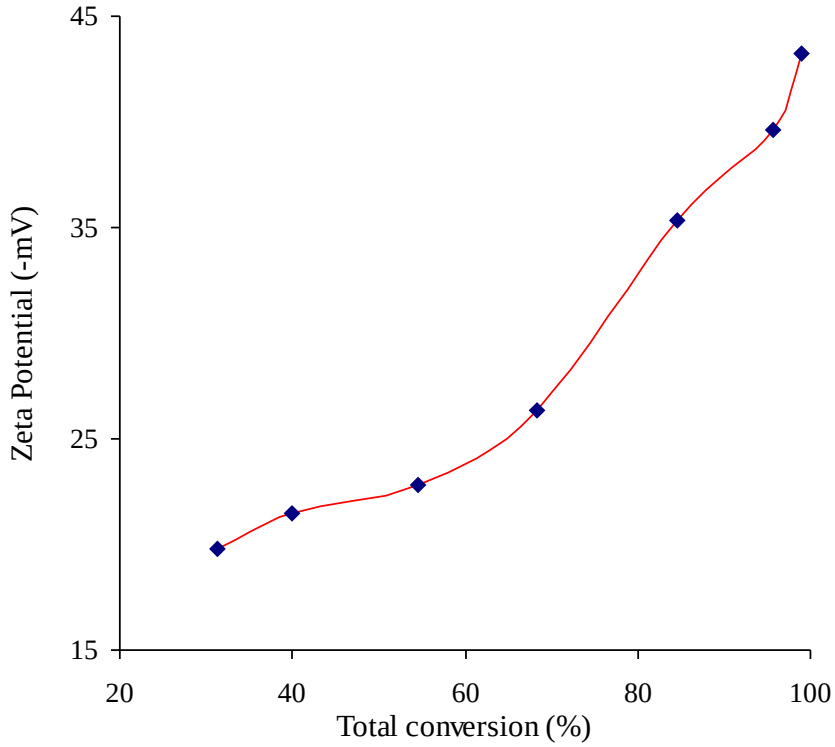


Figure 2.13. Zeta potential versus the total conversion for semicontinuous copolymerization of 3-MDG/BA; HV25 concentration was 5 g/l.

The propagation rate constants of 3-MDG and BA are 1265 and 2400 l mol^{-1} s^{-1} and their reactivity ratios are 1.94 and 0.54, respectively. Figure 2.14 shows the variation of the calculated average number of radicals per latex particle versus the overall conversion, depending on the type of surfactant. From the evolution of $\bar{n}$ values, two different behaviors were observed: (i) By using anionic surfactants, such as SDS and SLES, the average numbers of radicals per latex particle was approximately 0.3, which means that, in both cases, the polymerization follows the Smith–Ewart theory, case I. In case of using SDS and SLES (containing two ethylene oxide units), the particle sizes were around 55 nm. With these small sizes, the probability of radical coupling reactions within the polymer particles is very high. The average number of radicals per particle remained approximately 0.3 throughout the polymerization. By using NOS10 (containing 10 units of ethylene oxide with a sulfate end-group), the average value of radicals per particle changed and was found to be 1.3. This could be due to a lower surface charge density, leading to a secondary limited coagulation. (ii) By using the nonionic surfactant HV25, containing 25 units of ethylene oxide, the particles sizes are larger than 60 nm and appear to contain more than one radical. The $\bar{n}$ value increased at a conversion interval between 20 and 70% and then remained constant at the end of the polymerization, reaching an average value of 15. This behavior is tightly related to the

evolution of D and N_p, indicating that coagulation took place as the polymerization proceeded. So, the evolution of $\bar{n}$ (obviously different from 0.5) indicates that the copolymerization could, rather, follow the Smith–Ewart kinetic, case III.

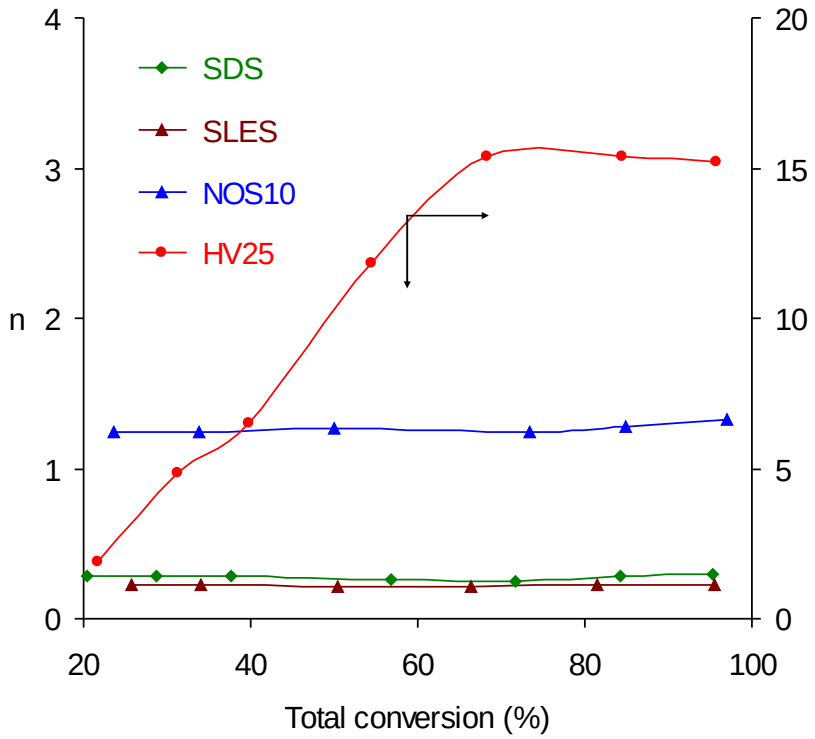
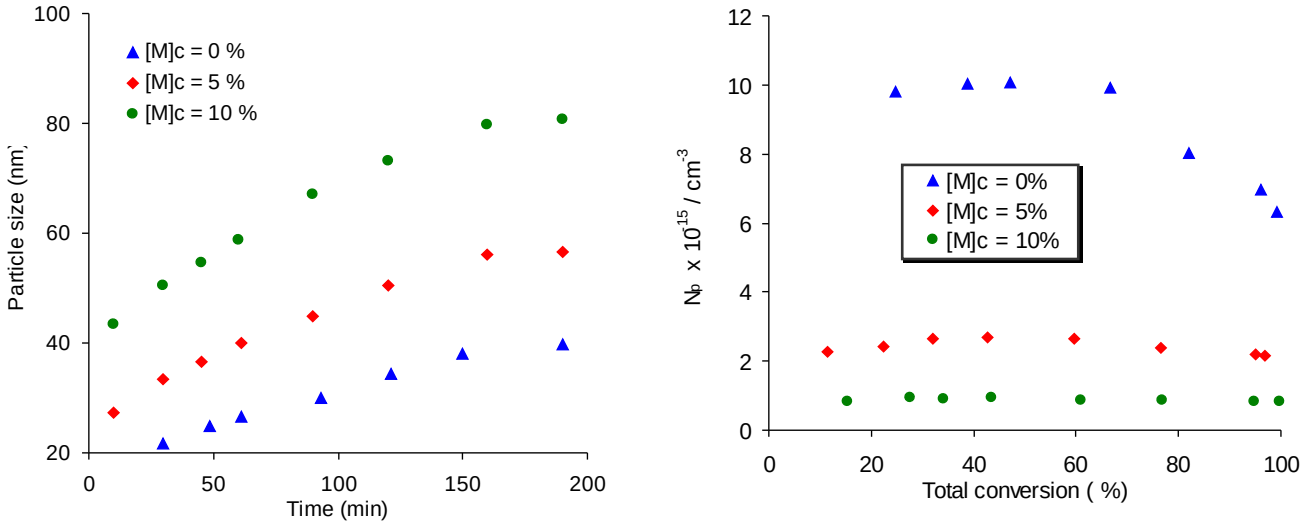


Figure 2.14. Effect of the type of surfactant on the total average number of radicals per particle ($\bar{n}$) during the polymerization. The initial composition of 3-MDG/BA was 35/65 in mol.

2.4.4 Effect of Seed Stage on the Particle Growth

In batch process, the particle size can be controlled by varying the concentration of the surfactant and the initiator, since the control of the particle size distribution is quite difficult. The semicontinuous process offers the opportunity to control both, the particle size and its distribution, at a given surfactant and/or initiator concentration. When semicontinuous processes are performed without adding any monomer at the beginning of the reaction, they commonly suffer from the change of the particle number during the polymerization. So, it was recommended to add about 5-10% of the total monomer at the beginning of the reaction and allow its conversion being completed before starting to add the rest of the monomer(s). This precharge polymerization can be considered as a seed stage. The main aim of this step is to separate the nucleation and the particle-growth phases to enhance the colloidal stability. The time of this stage must be short to exclude the possibility of forming new particles during the

polymerization [10]. As shown in Figure 2.15, without seed stage, that is, without adding any monomer at the beginning of the reaction, the number of particles drops at about 60% conversion, which indicates a secondary coagulation. Contrarily, when 5 or 10% of the total monomers was added in the charge, N_p remained constant throughout the polymerization.



(a) (b)

Figure 2.15. Effect of the precharge on the size and the total number of particles´ evolution during semicontinuous copolymerization of 3-MDG/BA. $[M]_c$ refers to the weight percent of monomer mixture in the precharge, based on the total amount of monomers.

Table 2.4. Effect of the pre-charge in the semicontinuous emulsion polymerization on the final particle sizes and PDI.

Monomer in the pre-charge (wt %)	Particle Size (nm)		PDI
	calculated	found	
0	-	39.7	0.128
5	55.5	56.6	0.097
10	81.0	80.8	0.064

Furthermore, the PDI was narrower as the precharge amount increased. The final particle size can be predicted, in case of using the seed stage, according to the following equation (2.9) [11]:

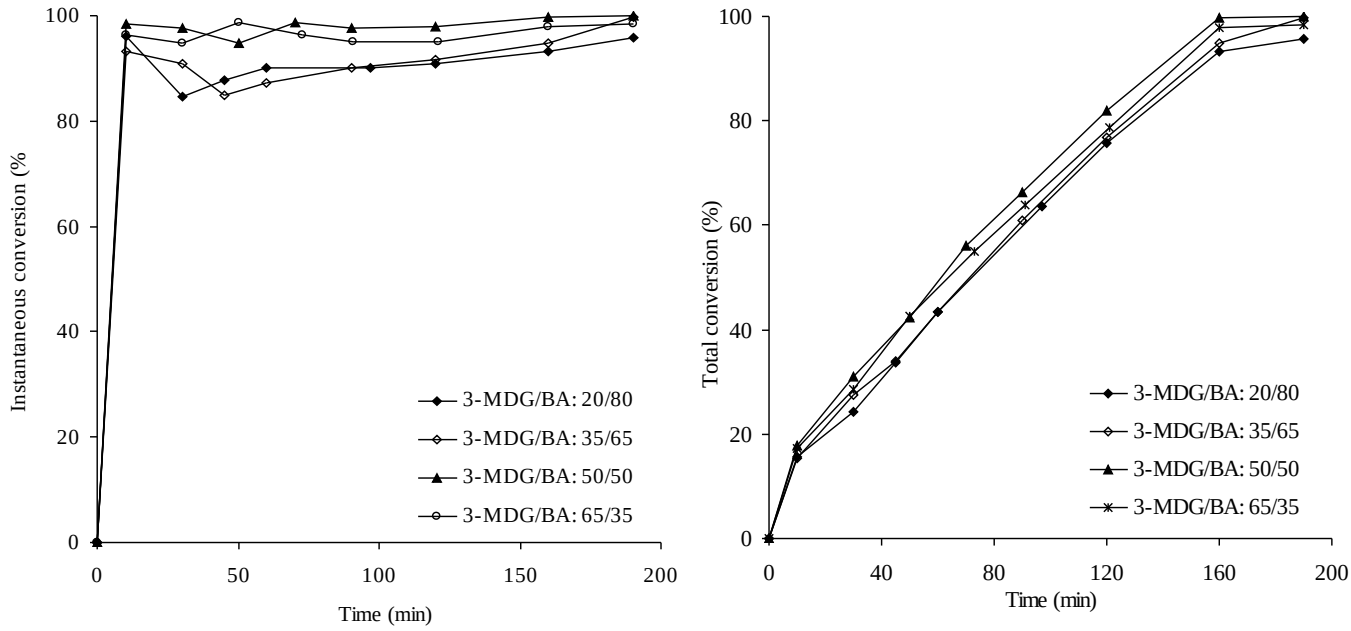
$$D_p = D_s [(W_s + W_1)/ W_s]^{1/3} \qquad (2.9)$$

where D_p is projected diameter of the final particle (nm), D_s, the seed particle size (nm), W_s, the seed polymer weight fraction; and W_1, the weight fraction polymer to be added on.
The calculated values from the experimental data show that this equation is applicable to our system, as can be seen in Table 2.4.

2.4.5 Effect of the Initial Monomer Composition

The reactivity ratios of 3-MDG and BA determined previously from the batch emulsion polymerization at 70°C were found to be $r_{3\text{-MDG}}$ = 1.94 and r_{BA}= 0.54, respectively. Copolymers made by batch polymerization exhibit, generally, a high composition drift, due to the difference in the reactivity ratios. The copolymers synthesized by the semicontinuous process under starved-feed conditions have compositions very close to the initial monomer feed compositions, because the monomer mixture completely polymerizes immediately upon entering the reactor. Figure 2.16 shows instantaneous and total conversions versus time at different initial monomer composition. At high BA ratios, instantaneous conversions are slightly lower than that with high 3-MDG ratios. The different initial monomer compositions have no remarkable effect on the total conversion. The production of latexes with a homogeneous copolymer composition improved the latex properties such as film formation. We followed the copolymer composition during and after the polymerization. It was found that the copolymer compositions were relatively similar to the initial monomer feed compositions. Furthermore, the variation of the 3-MDG ratio in the initial monomer feed has little influence on the particles size, particle-size distribution and the number of particles of the final latexes. As can be seen in Table 2.5, increasing the 3-MDG ratio from 20 to 65% in the feed led to a slightly decrease of the particle size from 63.5 to 58 nm and, consequently, increased the total number of particles from 1.44 to 1.99×10^{15} per cm^3. The lowering of the particle size by increasing the sugar content may be related to the high density of 3-MDG (1.19 g/l) in comparison to the density of BA (0.89 g/l). It was also found that the polydispersity and the T_g's of the final latexes increase with an increasing 3-MDG content in the feed. This may be related to the rigidity of the sugar monomer and to the softness of BA. At low sugar content, due to the low T_g of the copolymer, the newly formed particles are soft and coagulate and, consequently, the particle-size distribution widens. Contrarily, at a high sugar content, the T_g of the copolymer increased and the particles became harder, which hindered the Brownian collision, especially if the T_g was higher than the polymerization temperature. The feeding of monomer mixtures with the content of more than 70 mol % of

3-MDG was not possible, due to the recrystallization of 3-MDG at room temperature. So, the monomer feed-addition technique could be suitable for the 3-MDG/BA system at high 3-MDG content, if the temperature of the initial monomer mixture is maintained at about 40-45°C.



(a) (b)

Figure 2.16. Conversion-time curves of semicontinuous emulsion copolymerization of 3-MDG/BA with different initial monomer compositions, according to recipe described in Table 2.2; (a) instantaneous conversion; and (b) total conversion.

2.4.6 Effect of Solid Content on the Latex Stability

The production of latexes with a solid content over 50% is actually an industrial requirement. The syntheses of sugar latexes with high solid contents were investigated at 70°C using different surfactant types at various concentrations. As shown in Table 2.6, the preparation of sugar latex with about a 40% solid content using SDS as an ionic surfactant was carried out without any amount of coagulum. The coagulum (in wt percent) was determined by filtering a definite amount of latex through a cotton tissue sieve with 0.24-mm pore size. Then, the coagulum was dried and weighted. It was not possible, by the monomer addition technique, to prepare coagulum-free latex with a 50% solid content using anionic surfactant solely. Coagulum, 3.8%, was formed at the polymerization conditions reported in Table 2.6. High solid content sugar latexes (about 50%) were successfully synthesized using an equimolar mixture of an anionic and non-ionic surfactant, such as SDS and HV25. At a surfactant

concentration of more than 7.6%, based on monomers, a very low percentage of coagulum (<1%) was observed. Contrarily, using a surfactant concentration of 1.2% based on the monomer, a latex with 6.5% coagulum was obtained. From these results, it can be assumed that increasing the surfactant concentration reduces the coagulum. In all cases, polydisperse latexes were obtained, as seen in Table 2.6 (PDI between 0.15 and .20).

Table 2.5. Effect of the initial monomer feed composition in the semicontinuous emulsion polymerization of 3-MDG/BA on the final particle sizes (D), the PDI, the total number of particles (N_p), and the glass transition temperature (T_g).

3-MDG [a] (mol %)	Conversion (wt %)		3-MDG in copolymer [b]		D (nm)	$N_p \times 10^{-15}$ (cm^{-3})	PDI	T_g (°C)
20	40.1	99.7	0.20	0.21	63.5	1.44	0.064	14
35	38.6	99.6	0.35	0.36	63	1.58	0.080	43
50	41.0	99.6	0.50	0.51	61	1.76	0.097	69
65	40.8	99.8	0.66	0.65	58	1.99	0.129	99

a) An SDS conc. of 5 g/l was used and 10% from the monomers was added at the outset of the polymerization.
b) The sugar content in copolymer was determined from ^{1}H NMR.

Table 2.6. Latex stability at high solid contents prepared by semicontinuous emulsion polymerization of 3-MDG/BA (35/65) at 70°C using different surfactant types at various concentrations.

Solid content	Surfactant Type	Conc.[a] (wt %)	Conversion (wt %)	Coagulum (wt %)	D (nm)	PDI
40	SDS	4.4	99.7	< 0.5	73	0.190
50	SDS	4.4	99.5	3.8	76	0.183
50	SDS/HV25 (1 / 1)	1.2	98.9	6.5	128	0.156
50	SDS/HV25 (1 / 1)	7.6	99.3	<1	72	0.203

a) relative to monomers

2.5 CONCLUSIONS

Sugar latexes were prepared by semicontinuous emulsion copolymerization of 3-MDG and BA at 70°C, using the monomer feed-addition technique. Three pertinent parameters were found to play an important role on the kinetic behavior and on the colloidal and physical properties of the polymer latexes: (i) the monomer-addition rate, (ii) the type of the surfactant, and (iii) the concentration of the surfactant. The behavior of the sugar methacrylate (3-MDG) in the emulsion polymerization is similar to that of the other hydrophobic alkyl acrylate monomers. It was found that, under starved-feed conditions, the number of particles (N_p), the polymerization rate (R_p), the average molecular weight ($\overline{M}_w$) and the molecular weight distribution ($\overline{M}_w/\overline{M}_n$) are dependant on monomer-addition rate (R_m). It was also found that the type and concentration of the surfactant did not show any influence on the polymerization rate. However, their effect on the colloidal properties is marked. N_p remains constant during the entire polymerization, when an ionic surfactant is used. In case of a non-ionic surfactant such as HV25, a lower end number of particles and a greater size were obtained. A typical relationship was found among the surfactant concentration, particle size, and number of particles. At a low SDS concentration (below the CMC), D_p is high and N_p is small. As the SDS concentration increases, D_p decreases and N_p increases, following the classical theory of Smith-Ewart for hydrophobic monomers. Furthermore, the use of a seed stage leads to a narrow particle-size distribution and allows the formation of latexes with a defined particle size. It was also found that the increase of 3-MDG in the initial monomer composition enhances the PDI of the latexes and the T_g of the end copolymer. Finally, high solid content sugar latex was prepared with very low coagulum using a mixture of ionic and non-ionic surfactants.

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Chapter 3

Semicontinuous emulsion copolymerization 3-MDG/BA by pre-emulsion addition technique

3.1 Abstract

Semicontinuous emulsion copolymerization of 3-MDG/BA was investigated at 70 °C with the pre-emulsion addition technique. The effect of the emulsifier concentration and its distribution on the particle size (D) as well as on the evolution of the number of particles (N_p) during the polymerization was studied. The influence of the initiator concentration and its addition manner on the colloidal features was also investigated. The chemical stability and the properties of the sugar latexes were studied in the presence of sodium bicarbonate as buffer. The effect of the seed-stage on the particle size and its distribution was analyzed. The thermal, mechanical (such as film formation and stress-strain behavior), and rheological properties of the final sugar latexes were determined as well.

Keywords: pre-emulsion polymerization, sugar latexes, kinetic, latexes properties

3.2 Introduction

Pre-emulsion addition technique involves the separately feed to the reaction vessel of a pre-emulsion form, consisting of water, monomer(s), emulsifier and additives (buffer, transfer agent, etc.), concurrently with an initiator solution. The monomer(s) is well mixed with water, surfactant, and the additives and then the pre-emulsion is kept under stirring during the all addition period. An enormous variation in the particle size and particle size distribution can be obtained by choosing the addition strategy of each component to the reaction vessel. This variation in the colloidal features affects directly the rheological properties of the latexes, as well as the mechanical and thermal properties of the corresponding films.
We have presented in pervious chapter the monomer feed technique and we will expose here the main differences and similarities between the two techniques.

- From technical safety aspects, the pre-emulsion technique is favorable than the monomer addition, because during the addition a part of reaction heat will be cooled through the cold feed, which is bigger in case of pre-emulsion than that in case of monomer feed.
- In the pre-emulsion addition, the particle size is often larger than that prepared by monomer addition because the surfactant concentration by the latter process is usually higher at the beginning of polymerization. Furthermore, the end latexes prepared by pre-emulsion addition has lower polydispersity than those formed by monomer addition.
- The variable parameters in case of pre-emulsion addition are higher than those in the case of monomer feed.
- Monomer feed technique is easier to conduct than the pre-emulsion addition.
- By pre-emulsion addition, the covering of the particle surface by adsorbed surfactant is better than in case of monomer feed and batch process.
- By the two techniques, the addition rate affects the particle sizes and the polymer microstructure. Very low addition rate leads to decrease the concentration of monomers in the reaction loci, which in turn to decrease the molecular mass of polymer and enhance the crosslinking or branching reactions.

In this study, the effect of addition method of the initiator and emulsifier was investigated. Furthermore, the rheological properties of the latexes, as well as the mechanical and thermal properties of the corresponding films were analyzed.

3.3 Experimental

3.3.1 Materials

The sugar-bearing methacrylate monomer (3-MDG) prepared in our laboratory (appendix 1, p. 153). Butyl acrylate (BA; Fluka) was distilled just before use. Sodium lauryl sulfate (SDS; Merck), which has a critical micelle concentration (*CMC*) of 2.8 g/l, was used as an anionic emulsifier. Potassium persulfate (KPS, $K_2S_2O_8$) and sodium bicarbonate ($NaHCO_3$; Merck) were used as initiator and buffer, respectively.

Table 3.1. Recipe of semicontinuous emulsion copolymerization of 3-MDG/BA with the pre-emulsion addition technique.

	Charge (g)	Feed I (g)	Feed II (g)
Water	52	50	15
SDS	0.24*	0.96*	-
$Na_2S_2O_8$	0.012*	-	0.108*
3-MDG	-	17.40	-
BA	-	12.60	-

*) Other conditions will be given elsewhere.

3.3.2 Polymerization procedure

Semicontinuous emulsion polymerization was carried out at 70 °C in a 250 ml double wall glass reactor equipped with a glass stirrer, a reflux condenser, nitrogen inlet, temperature sensor, and sample device. The general polymerization recipe is given in Table 3.1. Amounts of the emulsifier, the initiator, and the buffer are given in Tables 3.2-3.5. The initial monomer ratio of 3-MDG/BA; 35/65 mol.%, which makes a copolymer with a T_g of 45 °C, was used in most polymerizations. A membrane pump (Stepdos 03 S, Type FEM03, from KNF Neuberger GmbH) was used to feed the pre-emulsion (feed I), and a titrating pump (Perfusor, type 100, from KD scientific Inc.) was used to feed the initiator solution (feed II). The initial reactor charge consisted of deionized, degassed water, part of the emulsifier, and 10% of the total amount of initiator. The reactor was charged under nitrogen atmosphere by water and the emulsifier and maintained under constant agitation of 175 rpm at 70 °C for 30 min. Some

polymerizations were carried out with the addition of 5-20% of the initial monomer amount in the pre-charge. The polymerization started with the addition of 10% of the initiator and then with feeding the reactor with the two feeds directly. The rate of the pre-emulsion feed was low enough (0.5 g/min) to ensure monomer-starved condition in the reactor. The addition time was 2.5 h, and the polymerization was continued in batch for another 30 min. Samples were taken at regular intervals to monitor the polymerization.

3.3.3 Characterization of the latexes

3.3.3.1 Monomer conversion, Particle size and particle size distribution were conducted as described before in chapter 2.

3.3.3.2 *Molecular weight and molecular weight distribution*. Molecular weight and its distribution were determined by gel-permeation chromatography (GPC) equipped with two columns (PLgel Mixed-B, Polymer Laboratories Inc.), multiangle laser light scattering (DAWN® DSP, Waytt Technology) and a refractive index (RID-6A, Shimadzu) detector. Chloroform (1ml/min) was used as eluent. The system was calibrated using the narrow dispersity polystyrene standard. The refractive index increment (*dn/dc*) of 3-MDG/BA copolymer was measured on a light-scattering photometer at 25 °C in chloroform, and at a wave length of 633 nm. The *dn/dc* of 3-MDG/BA copolymer with a composition 35/65 mol % was found to be 0.042 ml/g. The soluble part of the copolymer was extracted with chloroform using a Sohxlet apparatus. The gel content in the final copolymer was about 60-70%. The gel content was recovered by GPC from the difference between the injected and the collected masses and was similar to the value obtained by the extraction.

3.3.3.3 Mechanical and thermal properties

Latex films with a thickness of 0.8 mm were formed by casting the latexes at room temperature in molded silicone foils for two weeks. Mechanical measurements of the films were carried out at 25 °C. Some films specimens were heated at 50 and 100 °C for two hours and then measured at 25 °C. Static mechanical analyses (tensile strength measurements) of the films were performed using a universal testing machine (ZWICK 1445) with a testing speed of 200 mm/min. The measurements were carried out according to DIN (Deutsch Industry Norm) specification. The Young's modulus (E) was determined from the initial slope of the stress-strain curve. The energy of break, W_B, the energy per unit volume of the sample, was determined by the integration of the area under the stress-strain curve as in Eq. 3.1.

$$W_B = \int \sigma \, d\, \varepsilon \qquad (3.1)$$

where σ is the stress and ε is the strain.

The glass transition temperature (T_g) of the copolymers was performed on a differential scanning calorimeter (DSC-12E, Mettler-Toledo). About 10 mg dried copolymers were scanned at a heat rate of 20 °C/min. The T_g of the latex films was measured by calorimeter of the type TMA40, the Mettler Toledo star system.

The thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (TG/DTA 220 with disk station S200H Seiko, Tokyo, Japan). Circa 15 mg dried latex films were scanned at a heat rate of 20 °C/min in the range of 20 - 100 °C. Then the sample was held at 100 °C for 120 min (isothermal step).

TGA-FTIR measurements were performed by Mettler-Toledo on TGA 851^e in a nitrogen atmosphere with a heating rate of 5 °C/min and a temperature range of 25 - 350 °C.

3.3.3.4 Rheological properties

The rheological properties of the sugar latexes, such as the viscosity and the flow behavior, were measured at 20 °C by using Bohlin instruments with the cone-plate measuring system (CP 1°/40 mm). For very viscous samples, another cone-plate (CP 4°/40 mm) was used.

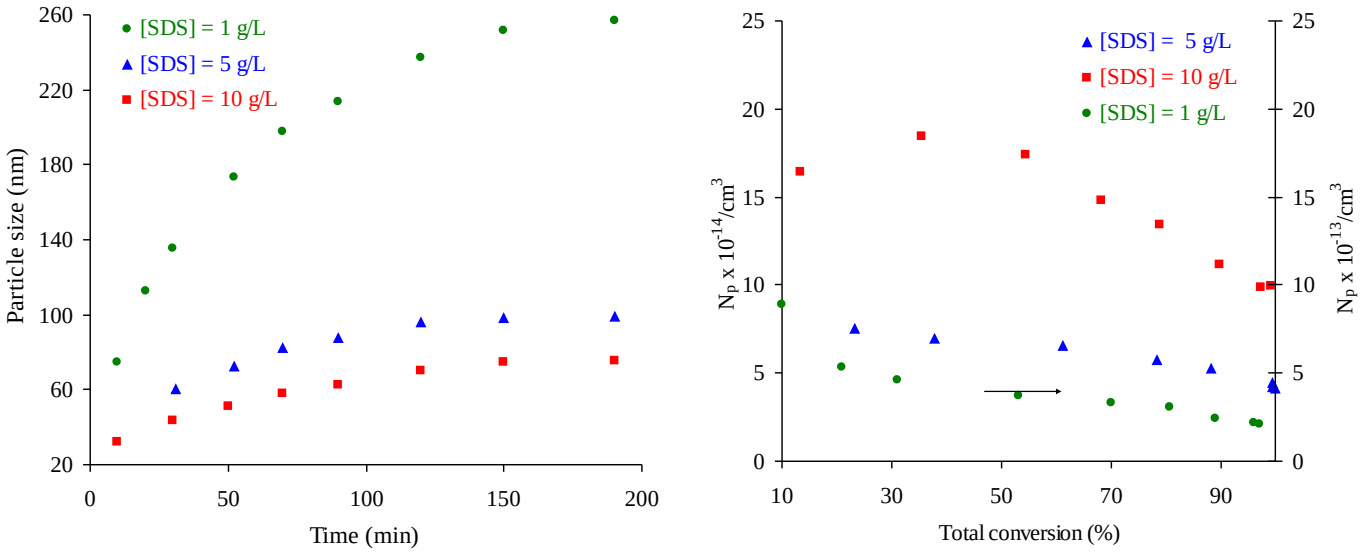
3.4 Results and Discussion

3.4.1 Kinetic studies

3.4.1.1 Effect of the emulsifier on the colloidal properties

Semicontinuous emulsion polymerization of some (meth)acrylate monomers was the topic of some investigations [1-3]. It was concluded that most of the (meth)acrylate monomers follow the homogenous nucleation mechanism, wherein the water solubility of the monomer and the ionic strength of the aqueous medium play a key role in the nucleation step.

In the semicontinuous emulsion polymerization, the emulsifier concentration and its addition strategy heavily influence the particle size (*D*) and its distribution (*PSD*). Sütterlin et al. [1] have reported about the semicontinuous emulsion polymerization of some (meth)acrylate monomers, such as BA, MMA, etc. They concluded that most of (meth)acrylate monomers followed the homogenous nucleation theory from Fitch and Roe, wherein the water solubility of the monomers plays a key role in the nucleation step. Šnupárek et al. [2, 3] has also studied the semicontinuous polymerization of some alkyl acrylates with different polarity and water solubility. They also found that the homogeneous nucleation was the most probable mechanism for particle formation.



(a) (b)

Figure 3.1. Semicontinuous copolymerization of 3-MDG/BA at different emulsifier concentrations. a) particle size evolution against time, b) total number of particles (N_p) against the total conversion.

Table 3.2. Conditions of semicontinuous emulsion copolymerization of 3-MDG/BA with different emulsifier concentrations and distributions, and characterization of the final sugar latexes.

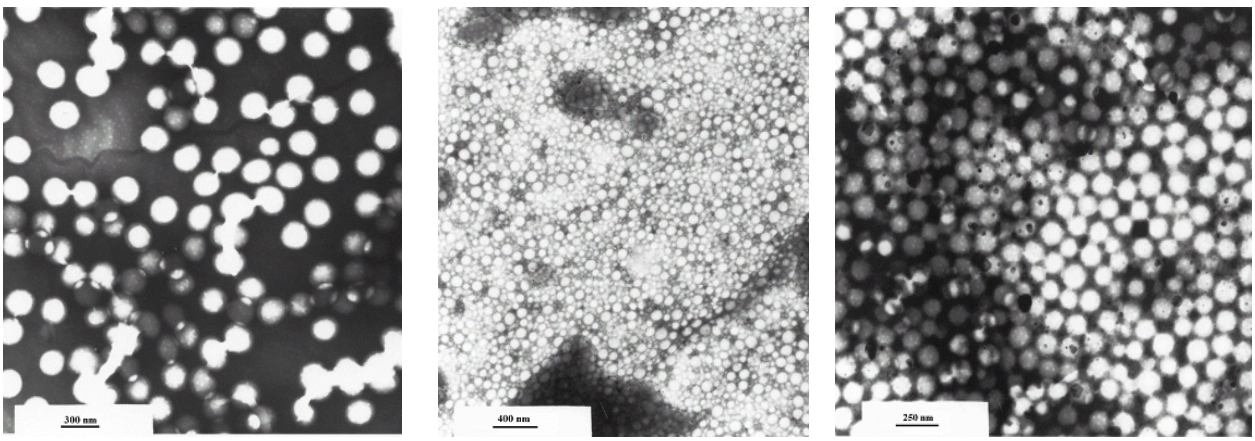
[SDS] (g/l)	1	5	10	10	10
SDS in charge (g)	0.06	0.12	0.24	0.6	1.2
E_c [a] (wt.%)	20	20	20	50	100
SDS in feed I (g)	0.24	0.48	0.96	0.6	-
E_E [b] (wt.%)	80	80	80	50	0
D [c] (nm)	257	99	75	59	40
PDI [d]	0.03	0.03	0.067	0.07	0.128
N_p [e].10^{-14} cm^{-3}	0.21	4.1	9.9	18.9	63.1
$\overline{M}_n.10^{-5}$ g /mol	1.6	2.7	3.9	2.6	7.9
$\overline{M}_w/\overline{M}_n$	1.6±0.4	1.4±0.4	3.1±0.3	1.4±0.5	1.4±0.4

a) E_c is the emulsifier concentration in the charge.

b) E_E is the emulsifier concentration in the pre-emulsion.

To study the effect of the emulsifier concentration on the colloidal properties of 3-MDG/BA, three semicontinuous emulsion polymerizations were conducted by varying the SDS concentration as in Table 3.2, at three levels; 1, 5, and 10 g/l. The emulsifier concentrations and their distributions between the reactor charge (E_c) and the pre-emulsion feed (E_E), as well as the characterization of the final sugar latexes are given in Table 3.2. The particle size evolution versus time is shown in Figure 3.1a. Also, the variation of the number of particle (N_p) versus conversion is shown in Figure 3.1b. At low [SDS], 1g/l, i.e. below the *CMC*, *D* increased rapidly throughout the polymerization. The homogenous nucleation is the predominant mechanism for particle formation in this case. The coalescence of smaller-sized particles within themselves or with existing particles (primary coagulation) leads to an increase in the particle size (257 nm) and a narrowing of the particle size distribution (*PDI* = 0.03). Contrarily, above *CMC*, the micellar and the homogenous nucleation participate together in the particle formation. When the emulsifier concentration increases, the stability of the new formed particles enhances, which in turn leads generally to the increase of the total number of particles. In the case of [SDS] of 5 g/l (approximately 2 x *CMC*), N_p remains relatively constant during the polymerization. At high [SDS], e.g. 10 g/l, N_p increases up to 30% conversion and then secondary coagulation occurs at about 50% of total conversion till

the end of polymerization (Fig. 3.1b). This could be related to the variation of the monomer/emulsifier ratio during the reaction. At the beginning of the reaction, this ratio is very low and consequently a huge number of particles are formed. The increase of the monomer (polymer)/emulsifier ratio during the feeding period leads to the decrease of the free emulsifier molecules, which are required to cover all these numbers of particles, so consequently, secondary coagulation occurs. As shown in Table 3.2, by increasing [SDS], the particle size distribution becomes broader. An exponent value of 1.7 was found for the final total number of particles versus [SDS]. It should be mentioned that this value is governed by the overall formulation and the way of its addition. The TEM-analysis of the 3-MDG/BA latex, prepared with [SDS] below the *CMC* (Fig. 3.2a), shows a narrow *PSD* and confirms that the sugar latex is monodisperse (*PDI* = 0.03).

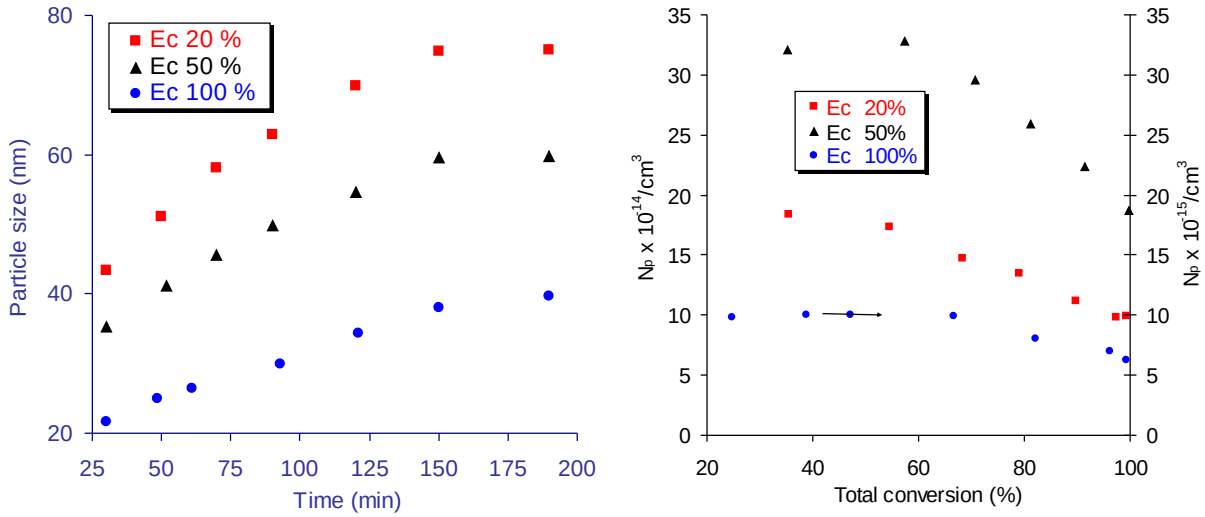


(a) **(b)** **(c)**

Figure 3.2. Electron-microscopy analysis of three 3-MDG/BA latexes formed under different conditions: a) [SDS] < CMC, b) [SDS] > CMC and without initiator in the charge; and c) by the addition of 20 % pre-emulsion in the the pre-charge.

Another interesting parameter which controls the colloidal features of the latex (*D*, *PSD* and N_p) is the emulsifier distribution between the charge and the pre-emulsion. To study the effect of the emulsifier addition method on *D* and N_p of 3-MDG/BA latex, three experiments were performed at a fixed [SDS] level of 10 g/l with a different distribution of SDS between the initial reactor charge (E_c) and the pre-emulsion (E_E), As shown in Table 3.2, the higher the concentration of emulsifier in the charge (E_c), the lower the final particle size and the higher the *PSD*. Fig. 3.3a, shows the evolution of *D* versus time as a function of E_c. A linear relationship was found between *D* and the polymerization time till the end of the addition time of the pre-emulsion (150 min). This is a typical profile for the periodical particle growth in the semicontinuous process. The evolution of N_p at different E_c versus the total conversion

(Fig. 3.3b) shows that N_p is approx. stable until about 60% of total conversion and then decreases gradually till the end of the addition time. It could be assumed that a secondary coagulation also took place at about 50% total conversion. A proportionality exponent of 1.13 was found between the total number of particles and the emulsifier concentration in the charge. From the previous results, 3-MDG/BA latexes with a wide different particle size and distribution can be prepared by adjusting the emulsifier concentration and its addition manner.



(a) (b)

Figure 3.3. Semicontinuous copolymerization of 3-MDG/BA at different emulsifier distributions between the charge and the pre-emulsion: a) particle size evolution against time, b) total number of particles (N_p) against the total conversion.

The average-molecular weight of a polymer and its distribution reflect the reactions, which occur during the polymerization. It is well known that most (meth)acrylate polymerizations in emulsion are accompanied by a high extent of crosslinking and branching, especially at high conversion. The gel content as indicator for the crosslinking was found to be about 50% for BA and BA/MMA (co)polymerization [4-6]. In semicontinuous polymerization, the high instantaneous conversion (over 95%), which is related to the fraction of the polymer in the particles, enhances the probability of chain transfer reaction onto BA units in the polymer and consequently leads to a crosslinked polymer. The gel content of 3-MDG/BA latexes was about 70%. As shown in Table 3.2, the number-average molecular weight ($\overline{M}_n$) of the soluble part of copolymers ranged between 1 to 8×10^5 g/mol. Concerning the soluble part, $\overline{M}_n$ increases by increasing N_p by means of increasing the emulsifier concentration in total or in the charge. The increase of $\overline{M}_n$ could be said to enhance the compartmentalization of the

radicals between the particles. The polydispersity ($\overline{M}_w/\overline{M}_n$) was in the range of 1.4 to 3.1. A clear prediction of the termination mechanisms is difficult, because the values of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ represent only about 30% of the total amount of the copolymer.

3.4.1.2 Effect of the initiator on the particles features

Water-soluble initiators such as persulfate salts are widely used in emulsion polymerization. It is well known that the total number of particles of the end latex as well as the rate of polymerization is directly proportional to the initiator concentration [I]. In batch polymerization, the initiator concentration plays the main role in the nucleation step. In semicontinuous emulsion polymerization, the nucleation step takes place during the entire polymerization and the dependence of N_p on [I] becomes quite different from that of batch process cases.

Table 3.3. Conditions and results of semicontinuous emulsion copolymerization of 3-MDG/BA at 70°C with different initiator concentrations and distributions.

[I][a] (wt.%)	0.2	0.4	1.2	0.4	0.4
$Na_2S_2O_8$ in charge (g)	--	--	--	0.012	0.06
$Na_2S_2O_8$ in feed II (g)	0.06	0.12	0.343	0.108	0.06
I_c [b](wt.%)	0	0	0	10	50
D [c] (nm)	117	99	85	75	58
PDI [d]	0.05	0.07	0.054	0.067	0.062
N_p [e].10^{-14} cm^{-3}	2.51	3.91	6.78	9.93	19.68
$\overline{M}_n$.10^{-5} g /mol	5.5	2.1	1.8	3.9	4.1
$\overline{M}_w/\overline{M}_n$	1.8±0.9	2.3±0.8	3.3±2.8	3.1±1.3	2.5±0.3

a) Initial initiator concentration, based on monomers.
b) I_c is the initiator concentration in the charge.

To study the effect of KPS as an initiator on the colloidal properties of the sugar latexes, three experiments were carried out with different KPS concentrations (see Tables 3.1 and 3.3). The polymerizations were conducted in the absence of the initiator in the charge.

The results in Table 3.3 show that the final particle size decreases with the increase of the KPS concentration. The number of particles is proportional to the 0.69^{th} power of [KPS]. This behavior is quite different from that found in the case of alkyl acrylate [1]. It was found that

N_p is inversely proportional to [KPS]. This phenomenon was interpreted by Sütterlin as an electrolyte effect on the stability of the oligoradicals and the primary particles. Increase of the electrolyte content in the aqueous phase enhances the primary coagulation and leads to a lower N_p [1]. Furthermore, the final *PSD* was not affected by the increase of KPS concentration. An average *PDI* value of 0.067 was obtained. Fig. 3.4a shows the time evolution of the particle size at various [I]. The particle size grows continuously throughout the polymerization, and this growth of the particle size is inversely proportional to the KPS concentration. At various KPS concentrations, N_p increases by increasing the conversion up to about 38% and then decreases again till the end of the polymerization (Fig. 3.4b). This trend is typical for the semicontinuous polymerization without monomer addition in the charge. Moreover, increasing the initiator concentration enhances the possibility of the secondary coagulation due to the decrease of the repulsive forces between the particles. The tendency of the coagulation became higher by increasing the initiator concentration.

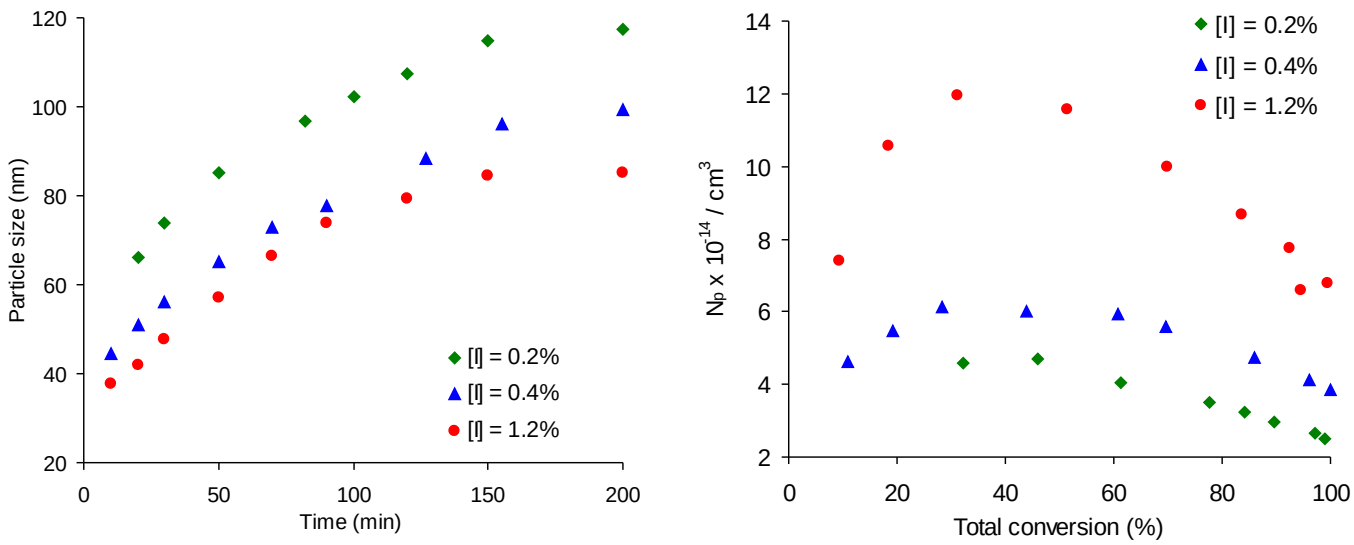
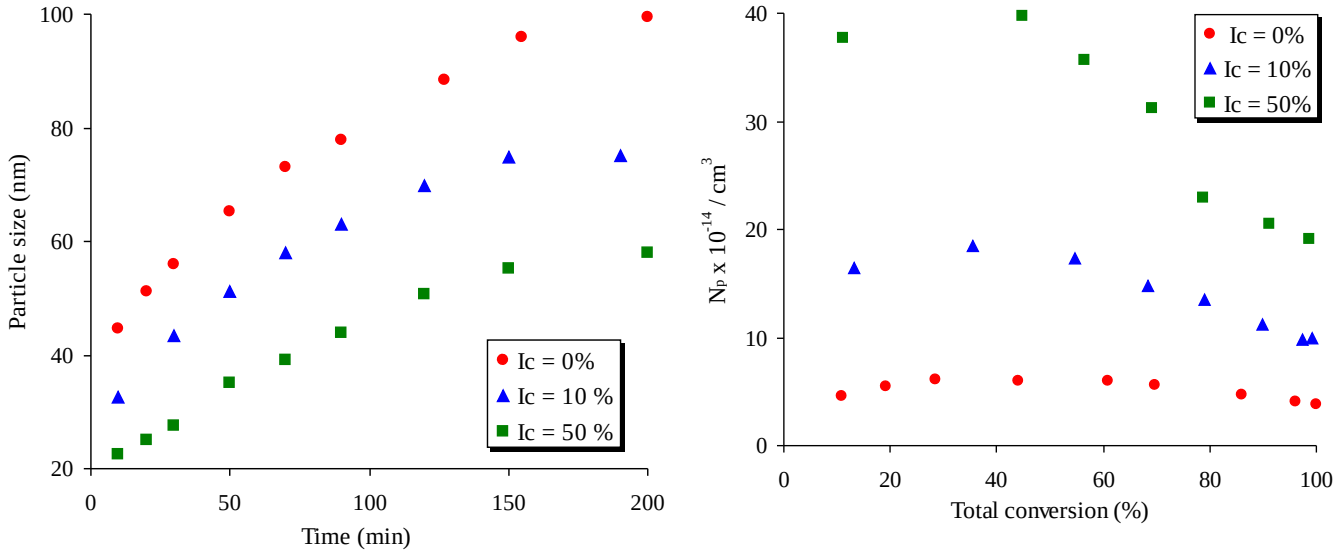


Figure 3.4. Semicontinuous copolymerization of 3-MDG/BA at different initiator concentrations: a) particle size evolution against time, b) the total number of particles (N_p) against the total conversion. [I] is the initiator concentration in wt% based on the total amount of monomer mixture.

At a fixed amount of initiator, the manner of initiator addition affects the particle size and distribution of the latex. As shown in Table 3.3, three polymerizations were conducted at a fixed [KPS] of 4% based on the total amount of the monomer with varying the initiator distribution between the pre-charge (I_c) and the feed II. Figure 3.5a shows the time evolution

of the particle size at various I_c. As the initiator concentration in the initial charge increases, the particle size of the latex decreases. Figure 3.5b shows the evolution of the number of particle versus conversion. A direct relationship between N_p of the end latex and I_c was observed. The tendency to secondary coagulation enhanced with increasing the initiator concentration in the charge. The final PSD narrowed slightly by enhancing the initiator concentration in the charge. Figure 3.2b illustrates the TEM-analysis of sugar latex prepared in the absence of KPS in the charge. The polydispersity of the end latex was 0.07, as a result of the QELS method. The above results show that the system 3-MDG/BA has little response to the variation of the ionic strength of the aqueous phase, at least in the range of the KPS concentration used in this study.

The number-average molecular weight of the soluble copolymers lies within the range of 2-6×10^5 g/mol and the polydispersity ranges between 1.5 to 3.1. The increase of $\overline{M}_n$ with an increase of I_c could be due to the increase of N_p, which in turn enhances the segregation of the polymer radicals into the particles. Without charging KPS in the pre-charge, $\overline{M}_n$ decreases with raising the KPS concentration. This could be related to enhance the termination reactions at high [I].



(a) (b)

Figure 3.5. Semicontinuous copolymerization of 3-MDG/BA at different initiator distributions between the charge and the pre-emulsion: a) particle size evolution against time, b) the total number of particles (N_p) against the total conversion.

3.4.1.3 Effect of buffer on the chemical and colloidal stability of the latexes

By the using of persulfate salts as initiators in the emulsion polymerizations decreases the pH-value during the polymerization (pH ≈ 3) due to the formation of acids in the aqueous media (Eq. 3.2-3.4):

$$S_2O_8^{2-} \rightarrow 2\ SO_4^{-\bullet} \qquad (3.2)$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH \qquad (3.3)$$

$$2\ {}^{\bullet}OH \rightarrow H_2O + 1/2\ O_2 \qquad (3.4)$$

Under acidic condition, some acrylate monomers such as BA may undergo hydrolysis reaction [7]. On the other side, the glucose protecting groups, isopropylidene groups, in 3-MDG can be cleaved under acidic conditions and at high temperature. The hydrolysis of the protecting groups of poly(3-MDG) in acidic aqueous media, such as formic, hydrochloric, sulfuric acids, and also by using acid ion exchange resins, was conducted to obtain a water soluble saccharide based polymers. The hydrolysis of acetal groups can be selectively depending on the pH of the reaction medium. In this study, our interest was focused on preparing hydrophobic sugar latexes.

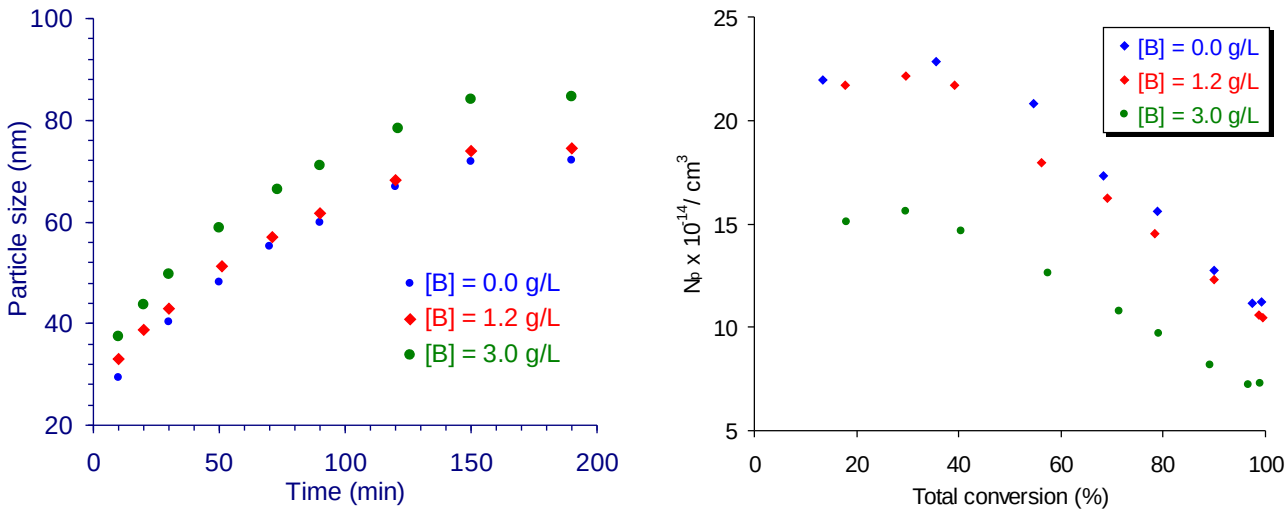


Figure 3.6. Semicontinuous copolymerization of 3-MDG/BA at different buffer concentrations: a) particle size evolution against time, b) total number of particles (N_p) against the total conversion. [*B*] refers to the buffer concentration in g/l.

By the first investigations of the chemical stability of the hydrophobic sugar moieties, according to the ^{1}H NMR and FTIR analyses, there was no indication of any hydrolysis of the protecting groups. Further analyses by gas chromatography showed that about 1.7 wt.% free acetone, based on the initial total amount of 3-MDG, was detected at the end of unbuffered polymerization. This low value indicates that only the protecting groups of the glucose on the surface of the latex particles could be hydrolyzed. By using $NaHCO_3$ as a buffer to avoid the hydrolysis of protecting groups, the content of acetone in the final latex was about 200 ppm. This indicates that the hydrolysis reaction of the protecting groups has been drastically reduced.

On the other hand, buffer as a salt could influence the latex stability and the mechanism of particle nucleation especially in the case of polar monomers such as VAc. As shown in Table 3.4, the variation of the buffer concentration has little effect on the final particle size and its distribution. The lowest particle size was obtained without buffer (72 nm), whereas 75 and 87 nm were obtained with 1.2 and 3.0 g/l $NaHCO_3$, respectively. The final *PDI* slightly decreases by increasing the buffer concentration. However all the sugar latexes are polydisperse (*PDI* >0.04). Fig. 3.6a shows the time evolution of the particle size at different buffer concentrations. There is no great effect on the final number of particles at a buffer concentration lower than 1.2 g/l. As the polymerization proceeds the particles size increases but in a lower extent in the presence of buffer. By increasing the buffer concentration up to 3 g/l, the particles size also markedly increases. Fig. 3.6b shows the evolution of the number of particles at various buffer concentrations versus conversion.

Table 3.4. Results of semicontinuous emulsion copolymerization of 3-MDG/BA at different buffer concentrations. Other conditions are according to recipe in Table 3.1.

[$NaHCO_3$] (g/l)	0	1.2	3.0
pH	2.97	7.3	7.7
D [a)](nm)	72	75	85
PDI [b)]	0.076	0.067	0.059
N_p [c)].10^{-14} cm^{-3}	9.93	10.44	6.65

Rudin et al. [8] have reported on the effect of the buffer and the initiator on the particles size of VAc/BA latexes and their distributions. They found that increasing of the ionic strength of the aqueous phase via addition of a buffer and/or initiator reduces the electrical energy of the repulsion, which in turn increases the particle size and widens the particle size distribution of

the latex. This behavior of 3-MDG/BA in emulsion polymerization is similar to other hydrophobic systems, such as styrene/BA. The ionic strength of the aqueous phase has no great effect on the colloidal stability.

3.4.1.4 Effect of monomer concentration in the pre-charge on the particle growth

Most of semicontinuous emulsion polymerizations are performed with polymerizing about 5-20% of the total monomers in batch form, a so-called in situ seed stage, before starting the feeding of the reactor to separate the nucleation and the growth phases. As shown in Fig. 3.7a, the latex prepared without the seed-stage has a smaller size than those carried out with it. The increase of particle size of end latex becomes more pronounced by the increase of the monomer concentration in the precharge. Furthermore, without the seed stage, the number of particles decreases during the polymerization, which indicated to the occurrence of a secondary coagulation of the polymer particles as mentioned before (Fig. 3.7b). In contrast, with addition of monomers in the precharge, a slight decrease of N_p is observed, which indicates a very limited secondary coagulation.

Table 3.5. Results of semicontinuous emulsion copolymerization of 3-MDG/BA at different precharge of pre-emulsion according to recipe in Table1.

$[M]_c$ in the pre-charge (wt.%)	0	10	20
Experimental *D* (nm)	75	112	136
Calculated *D* (nm)	-	112.3	133.5
PDI	0.067	0.042	0.024
N_p .10^{-14} cm^{-3}	9.93	2.93	1.68

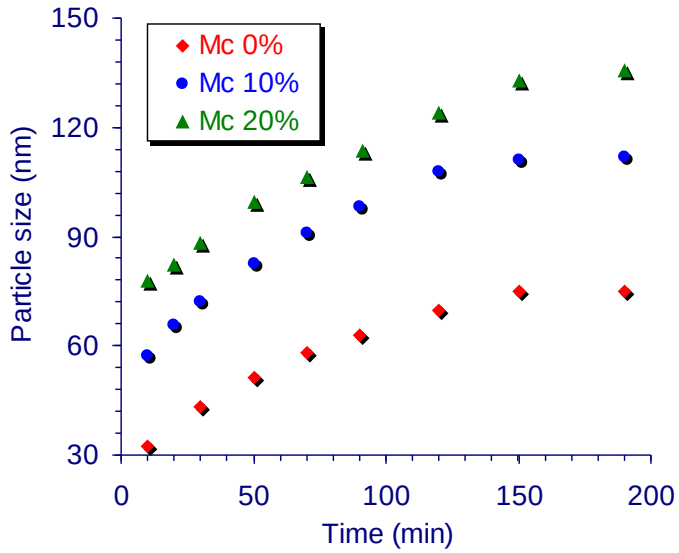
a) $[M]_c$ is the pre-emulsion as pre-charge in wt% based on the total amount of pre-emulsion.

The particle size distribution of the latexes (Table 3.5) becomes narrower with each increase of the amount of monomer in the pre-charge due to lowering the chance for formation of new particles as well as lowering secondary coagulation. Interestingly, a monodisperse sugar latex was obtained (*PDI* = 0.024) when 20% of the initial monomers were added in the precharge. The TEM-analysis of the sugar latex (Figure 3.2c) confirms the narrow *PDI*. In the absence of monomer in the precharge, the final sugar latexes are polydisperse (*PDI*>0.04). By using the

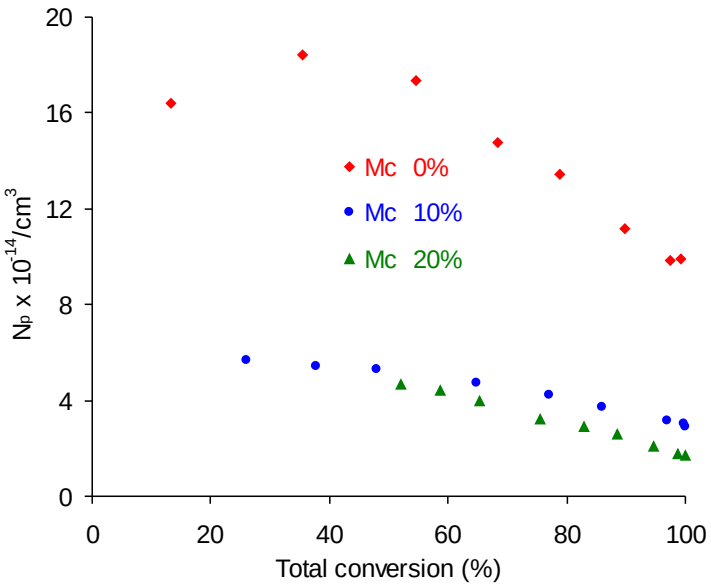
seed stage, the particle size of the end latex can be predicted according to the following Eq. 6:[8]

$$D_p = D_s\,[(Ws + W_1)/Ws]^{1/3} \qquad (3.6)$$

where D_p is the projected diameter of the final particle (nm); D_s, the particle size of seed; W_s, the weight fraction of seed polymer, and W_1, the weight fraction polymer to be added on. As shown in Table 3.5, the experimental particle size correlates with the calculated particle size.



(a)



(b)

Figure 3.7. Semicontinuous copolymerization of 3-MDG/BA at different amount of pre-charge: a) particle size evolution against time, b) total number of particles (N_p) against the total conversion. The polymerization condtions are given in Table 3.5.

3.4.2 Latexes properties

3.4.2.1 Thermal behavior

The glass transition temperature (T_g) of polymers is an important physical parameter for many applications. The T_g values of poly(3-MDG) and poly(BA) are 167 and –54 °C, respectively. The variation of the initial monomer compositions makes it is possible to prepare copolymers with a wide range of T_g. Experiments proved that 3-MDG/BA copolymers, prepared by a batch or semicontinuous process, showed only one T_g.

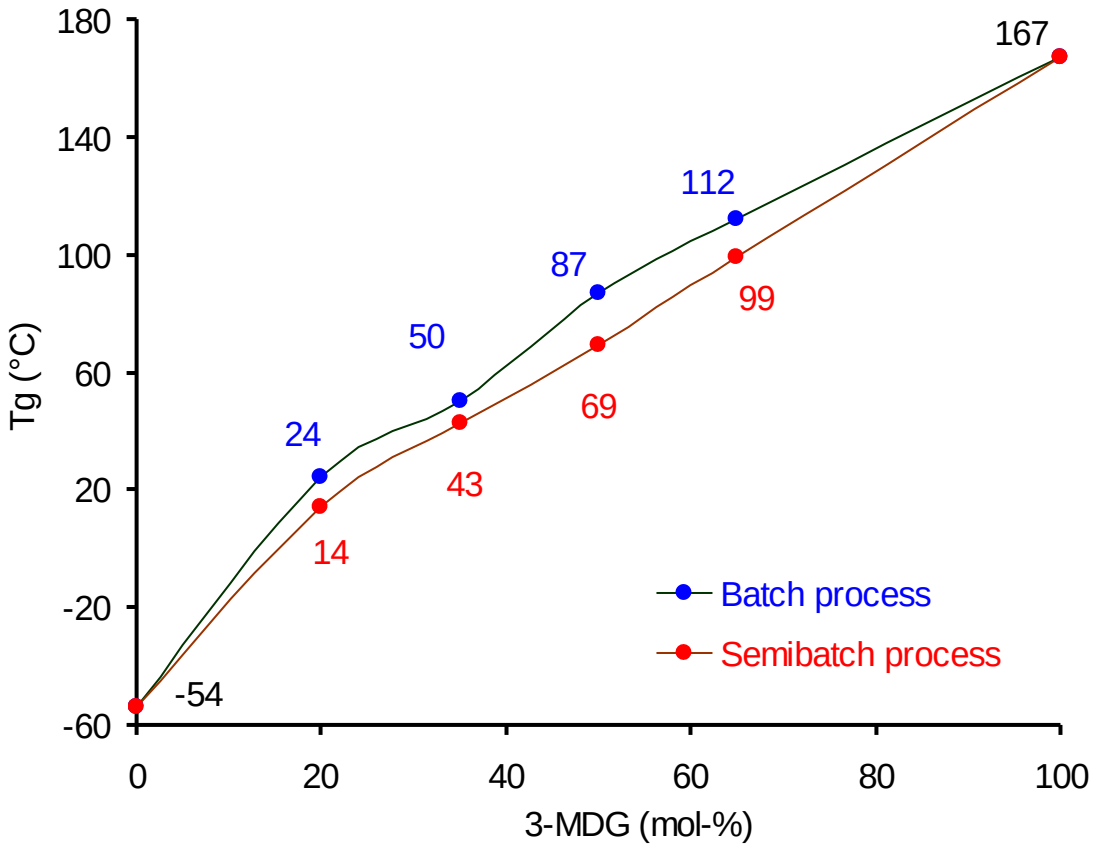


Figure 3.8. The influence of the type of the polymerization process on the glass transition temperature of the copolymers at different 3-MDG contents.

As shown in Figure 3.8, the T_g of the copolymers increases when the content of 3-MDG is enhanced in the initial monomer composition. Furthermore, the T_g's of batch latexes are generally higher than those of semicontinuous latexes. The difference in the glass transition temperature (ΔT_g) was about 8 °C at a low 3-MDG content, and about 15 °C at a high 3-MDG

content in the copolymers. This confirms the influence of the polymerization process on the glass transition temperature.

It should be mentioned that both monomers are hydrophobic and have the same water solubility (about 2 g/l at 60°C). However, they demonstrate different reactivity ratios, $r_{(3\text{-MDG})} = 1.94$ and $r_{(BA)} = 0.54$. This indicates that by a batch process, 3-MDG polymerizes faster than BA. The polymer composition drift is more pronounced in case of the batch process than in a semicontinuous process under starved-feed conditions. Thus, the most probable explanation for the difference in T_g is the difference in the microstructure of the copolymers. The low molecular weight of polymers prepared by semicontinuous process may also be a reason for the decrease of T_g. Furthermore, high instantaneous conversion of about 95% and a high polymerization temperature of 70 °C increase the branching level and the gel content in the produced polymer. This could be also the reason for the low T_g of semicontinuous polymers. Asua et al. reported on the seeded semicontinuous emulsion polymerization of BA and found that the branching level was about 2-4%. A different behavior was reported by Vanderhoff et al. [9, 10] for (VAc/BA) copolymers in which the monomers exhibit different polarities and water solubilities. They founded that the semicontinuous latexes display two different molecular weights 6.6×10^3 and 1.19×10^6 g/mol, respectively. They suggested that the presence of larger amount of the low-molecular weights in the semicontinuous latexes acted as plasticizer, which led to a lower T_g compared to the batch latexes.

Table 3.6. Comparison of the mechanical properties between the batch and semicontinuous latex films at different polymer compositions.

Copolymer composition (mol.%)	T [a)] (°C)	Young's modulus E (N/mm^2)		Energy of break W_B (N/mm^2)	
(3-MDG/BA)		Batch	Semicontinuous	Batch	Semicontinuous
20/80	25	3.31	2.61	463.3	405.4
20/80	50	14.74	4.60	863.6	535.8
20/80	100	27.23	11.98	132.9	71.6
35/65	51	27.7	11.7	-	-

a) T is the curing temperature at which the films have been treated, but all the measurements were performed at 25°C.

3.4.2.2 The formation of films and their mechanical properties

The formation of film from latex and its mechanical properties are important for specific applications, such as paints and coatings, adhesives, and paper industry. The mechanism of the film formation from latexes usually takes place in three consecutive major steps. First, evaporation of water brings the particles into a close contact. Then, the coalescence and the deformation of the particles take place. Finally, interdiffusion of polymer chains between adjacent particles occurs. It was found that the nature of the emulsion polymerization process affects the properties of the formed films [10].

In order to study the properties of sugar-containing films, 3-MDG/BA latexes with a composition of 20/80 and 35/65 mol.% were prepared as stated in the recipe in Table 1. The films were prepared at room temperature. Some specimens of the films were heated at 50 and 100 °C for two hours in order to study the effect of curing temperature on film properties. As shown in Table 3.6, the Young's modulus (E) and also the fracture energy (W_B) are higher for films prepared from the batch latexes than those from semicontinuous ones.

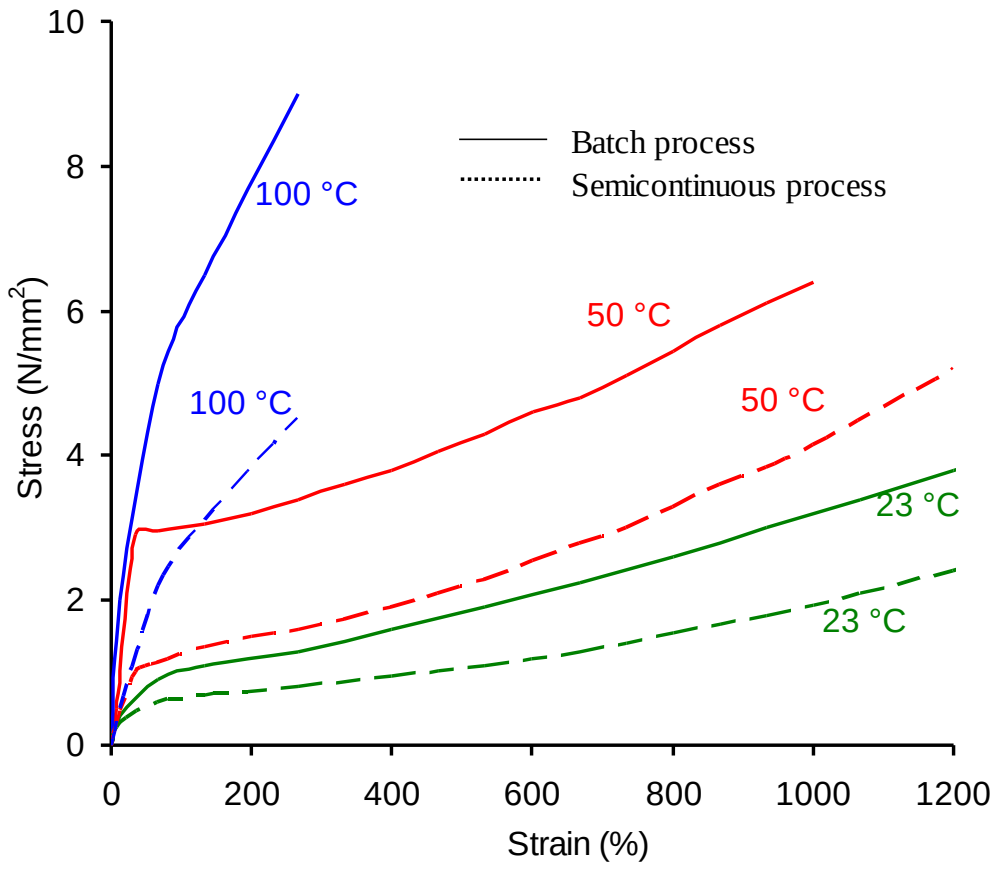
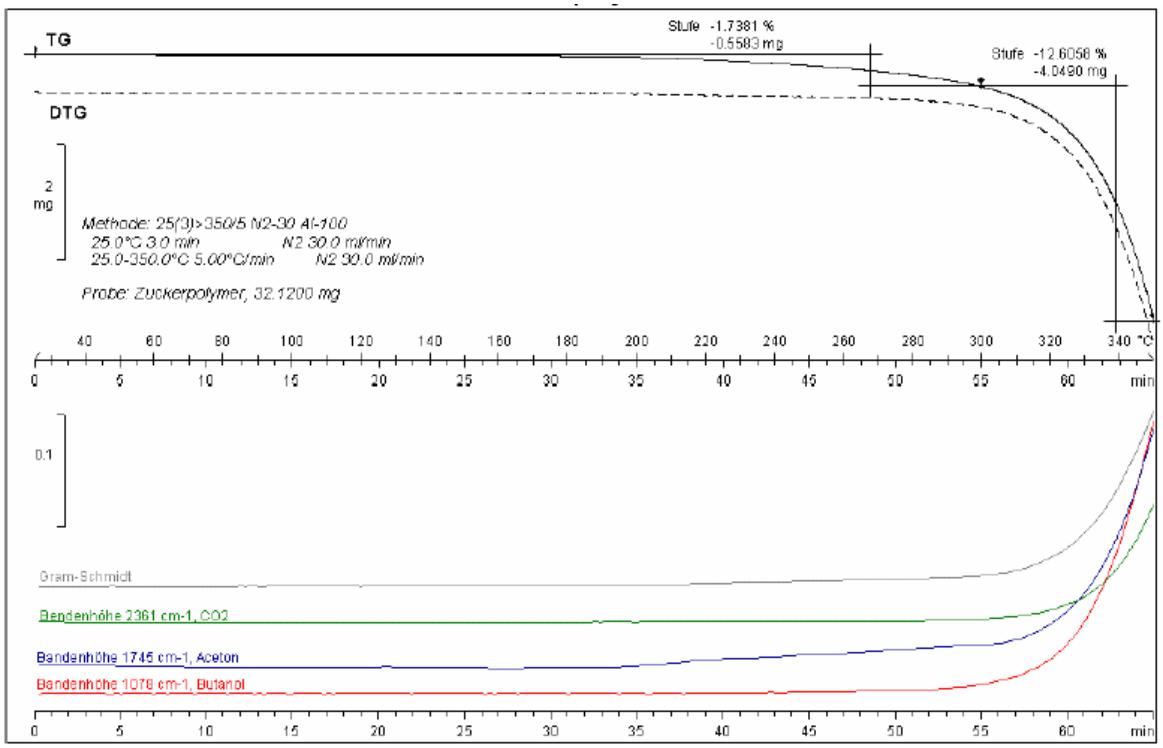


Figure 3.9. Effect of the polymerization process on the mechanical properties of some latex films prepared at 25°C and then annealed for 2 h at 50 and 100 °C. The initial monomer composition of 3-MDG/BA was (20/80 mol%).

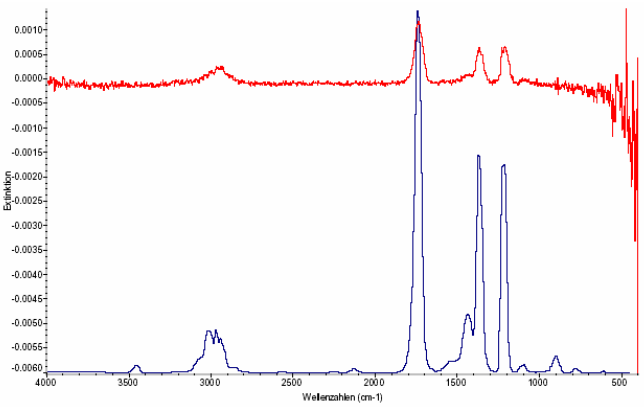
The different E and W_B-values between the batch and semicontinuous films may be ascribed to the drift of copolymer composition of the batch one, and/or to the difference in the colloidal properties of the end latex. For both types of 20/80-latex films, the Young's modulus increased by increasing the annealing temperature. At high temperature, interdiffusion of chain segments is favorable and crosslinking may also occur after the film formation. So, the fracture energy at 100 °C suddenly decreased and the films became more brittle. Furthermore, E and W_b are strongly dependent on the sugar content in the latex. At the same annealing temperature (50 °C), the enhancement of the sugar content in the both types of latex films from 20 to 35 mol.% increases the Young's modulus by a factor 2, and the film containing 35 mol.% 3-MDG was more brittle.

Figure 3.9 shows the stress-strain curves of the latex films heated at different temperatures. The measurements performed at 25 °C (above the T_g) are typical for thermoplastics in which the films undergo large, reversible deformations (elongations) at relatively low constraints (stresses). As the films were cured at 50 °C, the curves´ evolution changed and become typical for elastomers. At 100 °C, the curves rather showed a behavior similar to rigid plastics due to the high rigidity and high resistance to deformation. The change in mechanical behavior indicates that reticulation takes place. It should be noted that the sugar derivatives are not thermally stable at high temperatures (generally higher than 100-130 °C) and could decompose.

To determine the effect of a heating treatment on the latex films, some thermogravimetric analyses (TGA) were performed (see Figure 3.10a, b, and c). From the TGA analyses, about 1-2 wt.% of the film weight was lost after 2 h at 100 °C. This may be due to the evaporation of the rest of any water or to a very limited thermal decomposition of the polymer film. To determine the reason and the chemical nature of the weight loss, further measurements with a TGA-FTIR were carried out on pure polymers. The decomposition of 3-MDG/BA copolymer can be divided in two steps. In the first step, about 1.7 % weight loss at 200 °C in the form of acetone was occurred. The second decomposition step was around 350 °C having a weight loss of about 13 wt.%. In this step, beside acetone, butanol and carbon dioxide were detected. This indicates that the decomposition first started by the side chain and then the main chain. Further TGA tests on copolymers with different sugar contents were performed and identical curves were obtained. The films, with or without thermal treatment, are neither soluble in chloroform nor in acetone. The increase of T_g of the films from 24 to 38 °C after the thermal treatment may be ascribed to the evaporation of the rest of water or the cross-linkage reactions.



(a)



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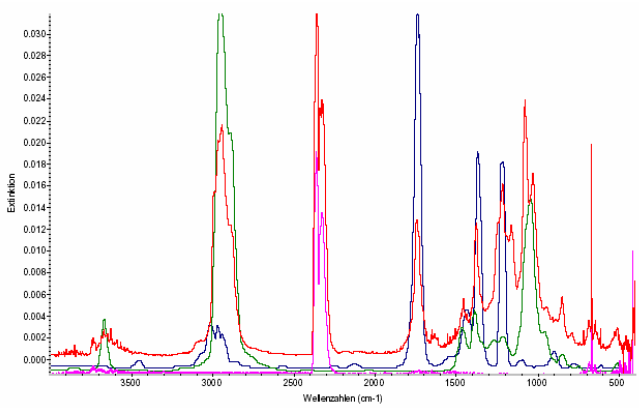

(c)

Figure 3.10. TGA-FTIR measurements on 3-MDG/BA copolymer with a composition of 20/80 mol.%; a) TGA diagram, b) FTIR-spectrum of the acetone as reference (blue line) and the sample (red line) at 200 °C, and c) FTIR-spectrum of the acetone (blue line), butanol (green line) and CO_2 (violet line) as references, and the sample (red line) at 350 °C.

3.4.2.3 Rheological behavior of the sugar latexes

There are many factors which can influence the flow behavior of the latexes. Generally, the latexes show either Newtonian or non-Newtonian flow. The solid content (*TS*), the particle size, and the particle size distribution of the latex are the main factors which affect the rheological behavior of an emulsion system. The influence of the solid content of the sugar latex on the flow behavior, as well as the relationship between the final viscosity and the corresponding *TS*, were studied. As shown in Fig. 3.11, relative diluted latexes with a solid content in the range of 20-30 wt.% show a Newtonian flow; the viscosity is constant against the shear rate. The concentrated sugar latexes (up to 50 wt.% solid content) show a shear thinning or pseudoplastic flow (non-Newtonian flow). Furthermore, Fig. 3.12 shows that the viscosity of the sugar latexes at very high shear rate increases exponentially when the solid content of the latex is increased. By enhancing the solid content of latex increase the interaction forces between the colloidal particles, leading to increase the viscosity.

$$\eta_{3000} = 0.639\ e^{0.0942\ TS} \qquad (3.7)$$

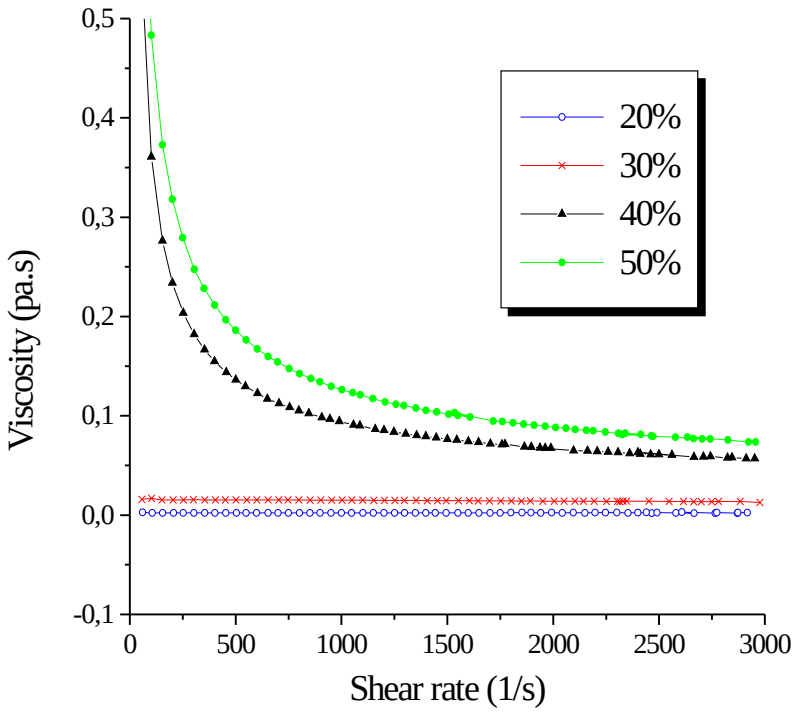

Figure 3.11. Evolution of the viscosity versus shear rate for sugar latexes at different solid contents. All other ingredients remained as described in Table 3.1.

The exponential equation, Eq. 3.7, was derived from Fig. 3.12 and can be used to calculate the shear viscosity of 3-MDG/BA latexes at a shear rate of 3000 s^{-1}. We think that this simple equation is only valid for the latexes of 3-MDG/BA. Using some additives, such as the addition of carboxyl containing monomers or viscosity modifiers during the preparation of 3-MDG/BA latexes, this equation will lose its validity.

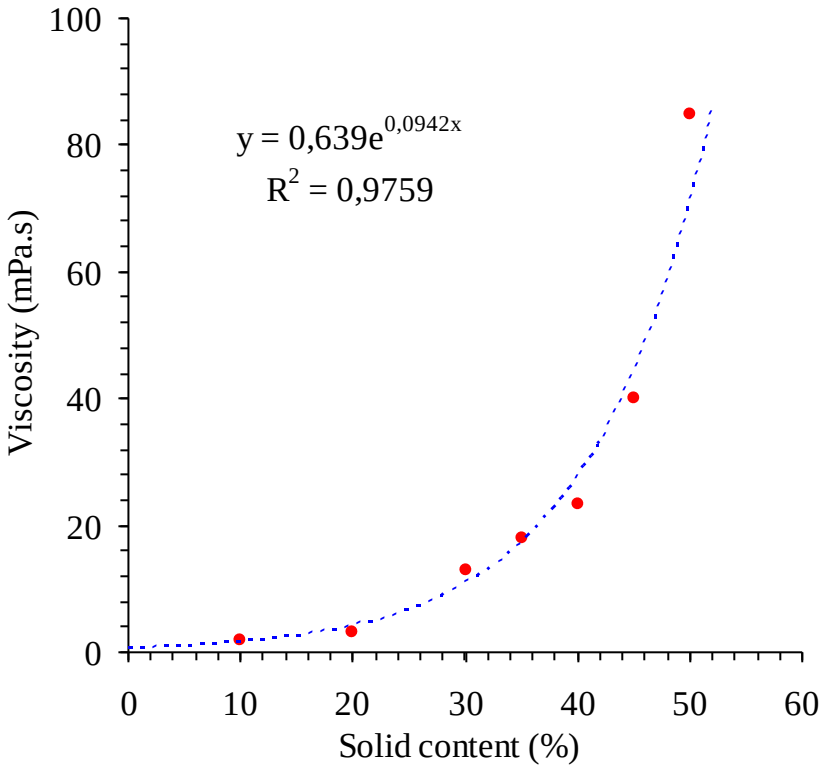

Figure 3.12. The influence of the solid content of the sugar latex on the viscosity, at high shear rate (3000 s^{-1}).

3.5 Conclusions

New type of latexes based on 3-MDG and BA were prepared by semicontinuous emulsion copolymerization with pre-emulsion addition technique. The effect of some parameters such as the emulsifier, initiator and buffer was investigated. The 3-NDG/BA system shows, in most cases, a behavior more similar to other hydrophobic systems. Increasing the emulsifier concentration, totally or in the charge, decreased the particle size and widened the particle size distribution. The initiator concentration and its distribution have a considerable effect on the particle size. With increasing the initiator totally or in the charge, *D* decreased and enhances N_p. The use of $NaHCO_3$ as a buffer suppressed the hydrolysis of the isopropylidene groups of 3-MDG. The concentration of $NaHCO_3$ below 1.2 g/l has no significant effect on the *D* and *PSD*. The ionic strength of the aqueous phase has no effect on the colloidal stability of 3-MDG/BA. Latexes with a defined particle size can be prepared by using the seed stage. The batch addition of a fraction of the total pre-emulsion at the outset of the reaction changes the properties of the end latexes. Increasing the batch fraction increased *D* and narrowed *PSD*. Tailor made polymers concerning the T_g value can be prepared by varying the initial composition of 3-MDG/BA. Furthermore, the type of the polymerization process also affects the mechanical and the thermal properties of the sugar latexes. The semicontinuous latexes have a lower T_g than the batch ones. Furthermore, the semicontinuous latex films have a lower Young's modulus as well as a lower fracture energy than the batch one. Regarding the rheological studies, the diluted latexes up to 25 wt.% solid content show Newtonian flow and the concentrated latexes show non-Newtonian flow.

3.6 References

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Chapter 4

Synthesis of Saccharidic Polymer Colloids via Free Radical Miniemulsion Polymerization

4.1 ABSTRACT:

Polymer colloids based on 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG) and butyl acrylate (BA) were prepared via free radical miniemulsion polymerization. The kinetic and colloidal features of the copolymerization were investigated. The final particle size (D) of the sugar latexes is inversely proportional to the concentration of the anionic emulsifier (Sodium dodecyl sulfate, SDS) and the nonionic one (alkyl polyglucoside, APG). It was also found that D is independent of the concentration of either the water-soluble initiator (KPS), or the oil-soluble initiator (AIBN). The rate of miniemulsion polymerization is lower in comparison with the conventional emulsion polymerization under the same conditions. The polymerization rate (R_p) and the total number of particles (N_p) are proportional to the 0.72^{th} and 0.93^{th} power of the SDS, and to the 1.40^{th} and 2.22^{th} of the APG concentration. Following reaction orders, 0.79/0.06 were obtained for R_p/N_p versus the concentration of KPS, and 0.22/-0.01 for AIBN, respectively.

4.2 INTRODUCTION

In this study, besides the use of 3-MDG, as glucose based monomer, we have also used a nonionic emulsifier based on glucose and fatty alcohols, such as alkyl polyglucoside (APG), in order to enhance the renewable portion in the formed latexes. The main advantages of APG are the biodegradability and the medical safety.

The miniemulsion polymerization is a new route to synthesize polymer colloids within a particle size range of 50 to 500 nm. The preparation of miniemulsion can be simply achieved by subjecting an oil/water mixture to a very high shear. The main feature of the miniemulsion polymerization is the monomer droplet nucleation, due to the high surface area of the monomer droplets.

In conventional emulsion polymerization, the emulsion systems are stabilized either electrostatically by using an ionic emulsifier such as sodium dodecyl sulfate (SDS), or sterically through nonionic emulsifiers, such as alkyl polyethylene glycols. This emulsion system normally suffers from the so-called Ostwald ripening process. This process refers to the diffusional degradation of small droplets to the larger ones. This phenomenon can be restrained by adding a costabilizer (hydrophobic agent) such as cetyl alcohol, hexadecane (HD), polystyrene, or poly-methyl methacrylate to the traditional ionic or nonionic emulsifiers. This stabilization system (emulsifier/costabilizer) drastically reduces the Ostwald ripening effect, giving the stability to the miniemulsion from some hours to some months, and enhances the possibility of monomer droplets nucleation.

Most of the previous works in miniemulsion polymerization were carried out on styrene (St), as model monomer, which has very low water solubility (0.3 g/l at 40 °C). Previous works have been done on copolymers such as VAc/BA, St/MMA, MMA/BA, and St/BA. It was found that a 1:1 droplets/particles copy cannot be achieved in all cases. The water solubility and/or the polarity of the monomer play a significant role in the mechanism of the nucleation of miniemulsion polymerization. Homogenous and micellar nucleation could be found parallel to the droplet nucleation especially under badly designed polymerization conditions. High emulsifier and/or initiator concentration, insufficient sonication time and also high water solubility of the monomer(s) could enhance the homogenous and/or micellar nucleation. In case of miniemulsion polymerization of MMA as relatively water soluble monomer, full droplet nucleation was achieved under the following conditions: relatively low emulsifier levels (10-20 mmol/l), high costabilizer levels (4% based on monomer), long sonication time (ca. 10 min), and low hold time (i.e. prior to initiator addition <10 min). Under these

conditions, the droplets were small (of the order of 100 nm), and the droplet nucleation was predominantly the nucleation mechanism [1].

The main advantages of miniemulsion polymerization can be summarized as follow: encapsulation of water-insoluble compounds such as pigments and inorganic salts in the latex particles, production of latexes with high solid content and low viscosity, controlling the particle size and their distributions, controlling the monomer composition in the reaction loci (monomer droplets), implementation of anionic and step polymerization in aqueous dispersed media, incorporation of hydrophobic monomers, and preparation of hybrid polymer particles. A more interesting advantage of miniemulsion polymerization is the possibility of controlling the molecular weight of the polymer, its distribution, and the polymer composition through its combination with a new technology, such as the living radical polymerization [e.g. stable free radical polymerization (SRRP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT)].

In this work, for the first time miniemulsion copolymerization of a binary system composed of a sugar monomer in the form of methacrylate (3-MDG) and an alkyl acrylate such as BA is presented. The influence of the most significant reaction parameters, such as the type and the concentration of both the emulsifier and the initiator, on the kinetic features and the molecular and colloidal properties of the end latexes will be reported. Finally, we have studied under which polymerization conditions a 1:1 droplets/particles copy is obtainable.

4.3 EXPERIMENTAL

4.3.1 Materials

The sugar monomer (3-MDG) was prepared from diacetone-D-glucose (Fluka) and methacrylic acid anhydride (Fluka). BA (Fluka) was distilled under reduced pressure just before use. Sodium dodecyl sulfate (SDS, Merck) as anionic emulsifier, and alkyl polyglycoside (APG), (Plantacare 2000 UP®, Cognis) as nonionic emulsifier, were used. APG was supplied as water solution with a solid content of 50 wt% and the molecular weight is approx. 390 g/mol. Hexadecane (HD, Aldrich) as hydrophobic costabilizer was used. All other ingredients were used as received. Potassium persulfate (KPS, Merck) and sodium bicarbonate ($NaHCO_3$, Merck) were used as initiator and buffer, respectively. The oil soluble initiator 2,2´-Azobisisobutyronitrile (AIBN, Fluka) was used without any purification.

4.3.2 Miniemulsion Polymerization of the Binary System 3-MDG/BA

To prepare the miniemulsion, 8.7 g of the fine powder 3-MDG was mixed with 6.3 g BA and 0.6 g HD. The initial monomer composition of 3-MDG/BA was 35/65 mol%, and was kept constant for all runs. This oily phase was mixed with 60 ml water solution containing 0.03 g $NaHCO_3$ and the required amount of emulsifier (SDS or APG). The concentrations of the emulsifier and the initiator were varied and the results are discussed. All concentrations are given in mol/l, i.e. mol per liter miniemulsion. The mixture was then stirred for 1 hr at room temperature under argon atmosphere. Then the miniemulsion was prepared by shearing the emulsion by means of ultrasonication for 5 min at 90 % amplitude with the "*Sonopuls*" homogenizer HD 2200 (from BANDELIN). In case of AIBN, as oil soluble initiator, it was mixed with the oil phase. In the case of KPS, the aqueous solution of the initiator was added prior to polymerization. The polymerization was carried out at 70 °C in a 100 ml double wall glass reactor equipped with a glass paddle-type stirrer, nitrogen inlet and sample device. All the polymerizations were stopped after 150 min reaction time. To monitor the polymerization, at least 10 samples were withdrawn from the reactor during the polymerization.

4.3.3 Characterization of the Latexes

4.3.3.1 Monomer Conversion

The conversion was determined gravimetrically as well as by gas chromatography (GC). GC analysis method has been described in chapter 2. The over all rate of polymerization (R_p) was calculated from the conversion-time curves at a conversion of about 20-25%.

4.3.3.2 Particle Size (D) and Particle Size Distribution

Particle size (D) and particle size distribution were measured by the quasi-elastic light scattering method (Zetasizer 3, from Malvern) as well as by transmission electron microscopy (TEM). For TEM analysis, the latex samples were highly diluted in aqueous solution of phosphotungstic acid (1%) as negative staining and were mounted on carbon coated copper grids. After that, the grids were dried at room temperature and then examined with a transmission electron microscope (Philips300). The polydispersity indexes (*PDI*) of the particle size distribution was determined from the light scattering measurements.

4.3.3.3 Surface Tension

The surface tension was measured on an interfacial tensiometer K8 (from KRÜSS) by using the Wilhelmy plate method. Approximately 25 ml of the miniemulsion was poured into a cleaned sample vessel with a diameter of 50 mm. The measurements were performed at a constant temperature of 20 °C. The surface tension value was the mean value from three measurements.

4.3.3.4 Calorimetric Measurements

The polymerization kinetics were investigated in a power compensation calorimetric unit. The polymerization was carried under isothermal conditions in a 500 ml glass reactor. The reactor temperature was adjusted to 60 °C to moderate the rate of polymerization and the jacket temperature to 44 °C.

4.3.3.5 Copolymer Composition

Copolymer composition was determined from ^{1}H NMR spectra, recorded on a "Bruker AM 400" spectrometer. The measurements were performed at room temperature, on polymer solution in $CDCl_{3,}$ containing tetramethylsilane as internal standard.

4.3.3.6 Molecular Weights

The weight-average molecular weights ($\overline{M}_w$) were determined with gel permeation chromatography (GPC) online with a multi-angle laser light scattering (MALLS) and refractive index detector. Polymer solution in chloroform, about 3 g/l, was analyzed at 25 °C using two columns (Plgel MIXED-B, particle size 10μm, length /I.D. 300×7.5 mm). The separation range of the columns is from 500 to 10^7 g/mol. Chloroform was used as eluent with a flow rate of 1 ml/min. The refractive index increment, *dn/dc*, of 3-MDG/BA copolymer was measured on a light-scattering photometer at 25 °C in chloroform, and at a wave length of 633 nm. The *dn/dc* of the copolymer (3-MDG/BA) (35/65 mol%) was found to be 0.042 ml/g.

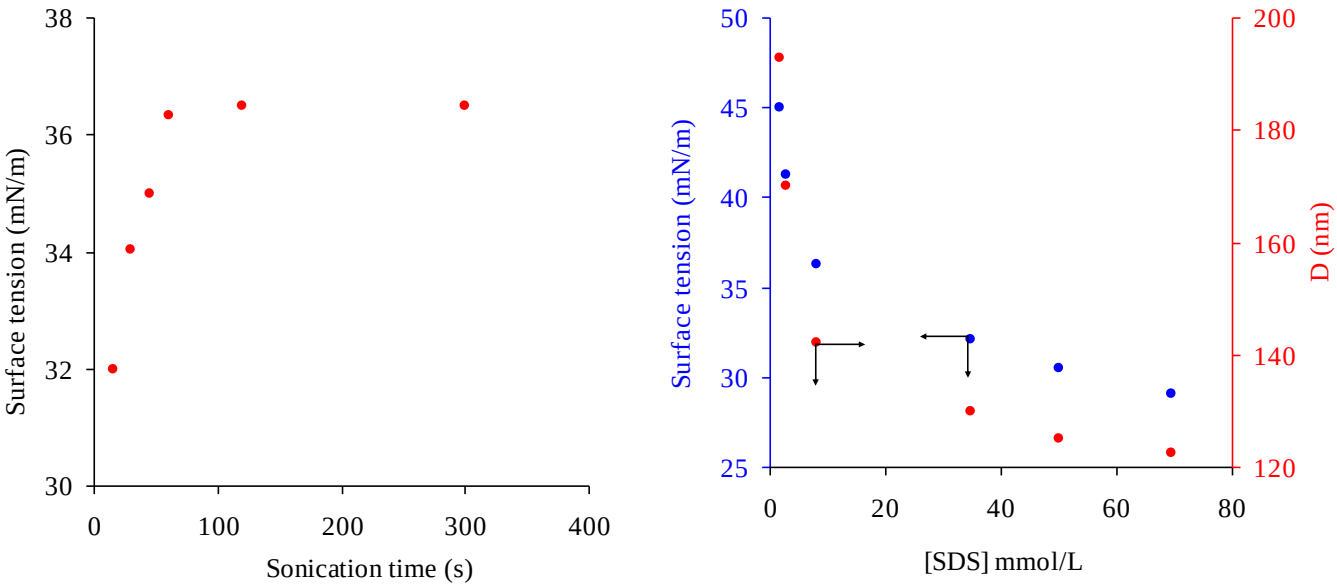
4.3.3.7 Thermal Properties

The glass transition temperature (T_g) of the copolymers was measured on a differential scanning calorimeter, series DSC-12E (Mettler-Toledo). About 10 mg of dried copolymer were scanned at a heat rate of 20 K/min.

4.4 RESULTS AND DISCUSSION

4.4.1 Preparation of the miniemulsion

Many miniemulsion systems in laboratory scale were prepared by the use of ultrasonication. It was found that the sonication time and/or the total energy input plays an important role in the efficiency of emulsification. Generally, the monomer-droplet size decreases with increasing the sonication power, the sonication time, and the amount of emulsifier, and increases with the volume fraction of the dispersed phase. The surface tension measurement, as a method to monitor the homogenization process, showed that a short sonication time, about 100 sec, was sufficient to obtain stable 3-MDG/BA miniemulsion. After a sonication time of 100 sec, the surface tension of the system increased from 28 mN/m, before ultrasonication, to 37 mN/m (Fig. 4.1a). The increase of the surface tension shows the increase of the total surface area of the droplets and shows also the incomplete coverage of the monomer droplets with the emulsifier.



(a) (b)

Figure 4.1. Surface tension of 3-MDG/BA miniemulsion as a function of the sonication time (a) and SDS concentration (b). Preparation of miniemulsion: 8.7 g 3-MDG, 6.4 g BA, 0.6 g HD, 0.34 g SDS (variable amount in Figure 4.1b), 0.03 g $NaHCO_3$, and 60 g of water. The sonication time in (b) was 5 min.

The dependence of the particle size on the emulsifier concentration, as it will be discussed in a later section, was analyzed by varying the emulsifier concentration. As demonstrated in

Fig. 4.1(b), a wide range of particle size can be realized by varying the emulsifier concentration. The particle size and surface tension decrease with increasing [SDS]. At an emulsifier concentration of 50 mmol/l or higher, the lowest average surface tension of 29 mN/m was obtained. This means that above this value, all the surface of the monomer droplets are covered with the emulsifier and new micelles are built in the system. This could enhance the micellar nucleation in the formation of polymer particles.

4.4.2 Effect of the type and concentration of the initiator

4.4.2.1 *KPS as water-soluble initiator*

Water-soluble initiators such as persulfate salts are widely used in emulsion polymerization. It is well known that in the conventional batch polymerization for hydrophobic monomers, the number of particles (N_p) and the rate of polymerization (R_p) are proportional to the 0.4^{th} power of the initiator concentration [I]. To study the effect of the initiator concentration, the kinetics of miniemulsion copolymerization of 3-MDG/BA was monitored by calorimetry (Table 4.2). From the heat flow rates versus time (Fig. 4.2), it can be assumed that: firstly, the total rate of conventional emulsion polymerization is faster than that of miniemulsion at the same conditions. This can be ascribed to the smaller particle size in conventional emulsion polymerization (65 nm) in comparison with that by miniemulsion polymerization (100 nm) (see Table 4.1). Nevertheless, the polymerization rate per particle in miniemulsion polymerization, $R_p/N_p = 4.1 \times 10^{-20}$ mol/sec, is faster than in the conventional one, 2.3×10^{-20} mol/sec, due to the high monomer concentration in the reaction loci and perhaps to the high average number of radicals per droplet. Secondly, the nucleation interval for both conventional and miniemulsion is very short (about 120 s) and similar for all KPS concentrations. Thirdly, the maximum rate of miniemulsion polymerization, which is calculated directly after the nucleation interval at about 20-25 % conversion, is dependent on the initiator concentration. The increase of the polymerization rate with the initiator concentration can be related to the increase of the number of radicals in the monomer droplets because the initiator concentration does not influence the particle size and consequently the number of monomer droplets (reaction loci). Finally, there is no signal for the gel effect as observed in the case of styrene miniemulsion polymerization [2]. This could be due to the small droplets size (100 nm).

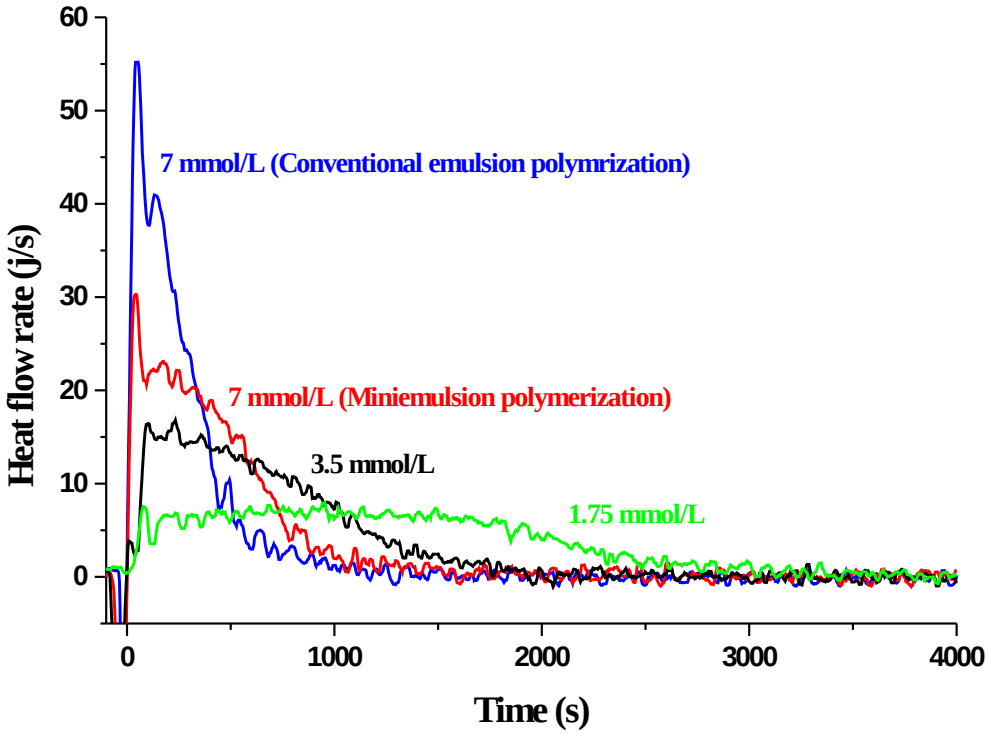


Figure 4.2. Kinetic study of miniemulsion copolymerization of 3-MDG/BA at different KPS concentrations by calorimetry. The polymerization conditions are given in Table 4.1.

As illustrated in Table 4.1, the variation of [KPS] does not affect the colloidal features (*D* and N_p), but enhances the rate of polymerization. At different [KPS], an average final particle size of 98 nm was obtained. At low [KPS], the low conversion of 75% after 150 min shows the limit of [KPS].

The double logarithmic plot of N_p versus [KPS] shows that N_p is proportional to the 0.06^{th} power of the initiator concentration (Fig. 4.3). This value indicates that a large fraction of the monomer droplets is successfully nucleated. This reaction order is not similar to the value found by conventional batch emulsion polymerization of 3-MDG/BA ($Np \propto [I]^{0.28}$) [3]. It should be noted here that this correlation is only valid in the used concentration range of KPS. Out of the used range, deviation can occur as found in the case of styrene miniemulsion polymerization [2].

Table 4.1. Effect of KPS and AIBN on the miniemulsion copolymerization of 3-MDG/BA.

Initiator type /concentration		D [a] (nm)	PDI [b]	N_p [c] (10^{14}/cm^3)	R_p [d] (10^{-3} mol/L . s)	Final conv. (wt %)	$\overline{M}_w$ [e] (10^6 g/mol)	$\overline{M}_w/\overline{M}_n$ [f]	Gel content (wt %)
KPS	(1.75 mmol/l)	103	0.035	1.84	2.54	75	1.95	1.4±0.1	59
	(3.5 mmol/l)	96	0.039	2.27	5.82	97.8	1.79	1.4±0.3	70
	(7.0 mmol/l)	98	0.033	2.01	8.42	98.4	2.22	1.5±0.1	83
	(7.0 [g] mmol/l)	65	0.04	3.01	15.35	98.4	1.04	1.4±0.2	75
	(10.5 mmol/l)	100	0.059	2.02	10.08	99	0.92	1.5±0.2	91
	(17.66 mmol/l)	96	0.060	2.27	17.0	99.5	-	-	-
	(7.0 [h] mmol/l)	110	0.07	2,69	5.69	99.6	0.98	1.5±0.2	80
AIBN	(4.06 mmol/l)	158	0.12	1.7	2.8	68.63	1.68	1.4±0.2	4
	(13.9 mmol/l)	132	0.090	1.75	3.5	98.5	3.25	1.5±0.1	3
	(19.95 mmol/l)	130	0.111	1.82	4.75	99.2	2.98	1.4±0.1	0.5
	(56.84 mmol/l)	133	0.122	1.73	5.67	99.9	2.18	1.4±0.2	1.0

Reaction conditions for KPS: 22.3 g 3-MDG, 16.1 g BA, 1.6 g HD, 0.9 g SDS, 0.6 g $NaHCO_3$, 360 g of water, and polymerization temperature = 60°C.

Reaction conditions for AIBN: 8.7 g 3-MDG, 6.4 g BA, 0.6 g HD, 0.34 g SDS, 0.03 g $NaHCO_3$, 60 g of water, and polymerization temperature = 70°C.

[a] D is the final particle size. [b] PDI is the polydispersity index. [c] N_p is the final number of particles. [d] R_p is the rate of polymerization after the nucleation stage (ca. 20-25%).

[e] M_w is the weight-average molecular weights. [f] M_w/M_n is the ratio of the weight- to number –average molecular weight.

[g] Conventional emulsion polymerization (without sonication). [h] The polymerization condition is the same as with AIBN (solid content = 20% and temperature = 70 °C)

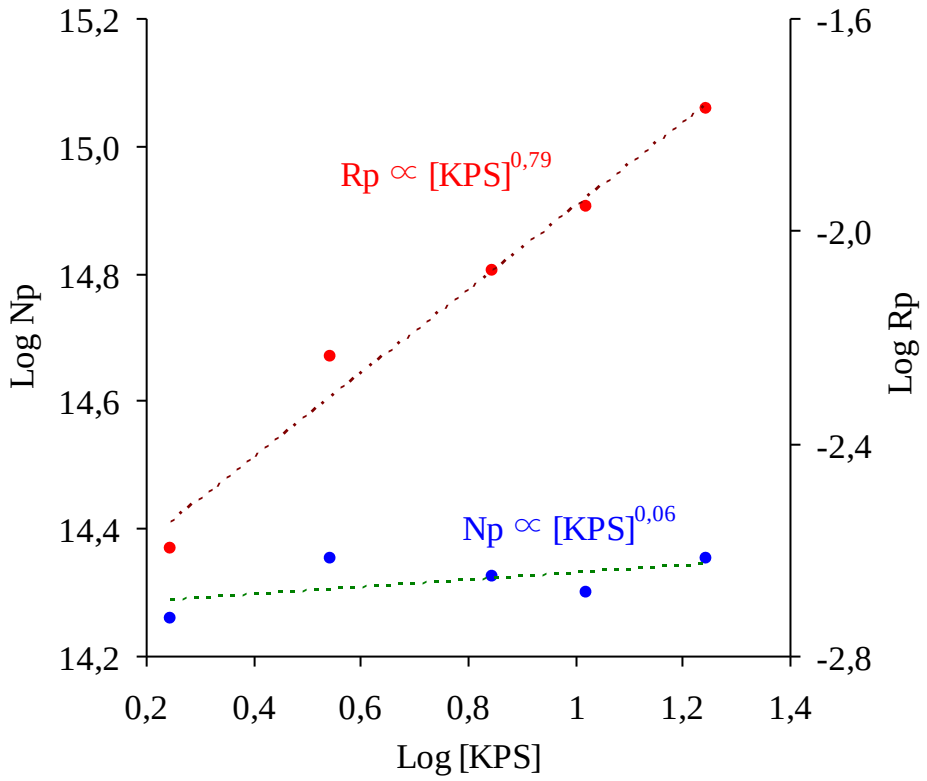


Figure 4.3. Influence of KPS concentration on N_p (•) and R_p (•) in miniemulsion copolymerization of 3-MDG/BA at 70 °C with [SDS] of 15.6 mmol/l.

The ratio of the final number of particles to the initial number of monomer droplets ($N_{p,f}/N_{p,i}$) could be an important parameter to estimate the nucleation mechanism in miniemulsion polymerization. When the value of this ratio is around unity, droplets nucleation could be the dominant mechanism. A low value can be an indication of incomplete droplets nucleation or coalescence. On the contrary, a higher value may be a signal to competition of other mechanisms such as micellar or homogeneous nucleation. It is worth pointing out that the light scattering method to measure the droplet and particle size is not the best and accurate method but it is the easiest one. The calculated ratio for this series of polymerization with KPS was around unity which indicates to the droplet nucleation.

The PDI values at different initiator concentration were below 0.04, which indicates a narrow particle size distribution (monodisperse latexes), and fortifies the probability of the monomer droplet nucleation as a main nucleation mechanism. As illustrated in Fig. 4.3, the relation between R_p and [KPS] shows a dependence value of 0.79. This correlation value is higher than that by conventional emulsion polymerization and could be related to the increase of the rate of radical entry to monomer droplets with increasing the initiator concentration. Figure 4.4 presents the individual conversions of 3-MDG and BA versus time. Due to the higher

reactivity of 3-MDG ($r_{3\text{-MDG}}$ = 1.94) over BA (r_{BA} = 0.54), 3-MDG polymerizes faster and the copolymer composition at the beginning is richer with 3-MDG up to about 70% total conversion. The change in the polymer composition during the polymerization is also verified by the measurement of T_g values (Fig. 4.5). The copolymer in the first phase has a T_g value of about 98 °C, then the T_g reduces with increasing the conversion till the end of polymerization (T_g = 50 °C). This composition drift cannot be overcome under these reaction conditions (droplet nucleation), because each droplet polymerized as a separated nanoreactor.

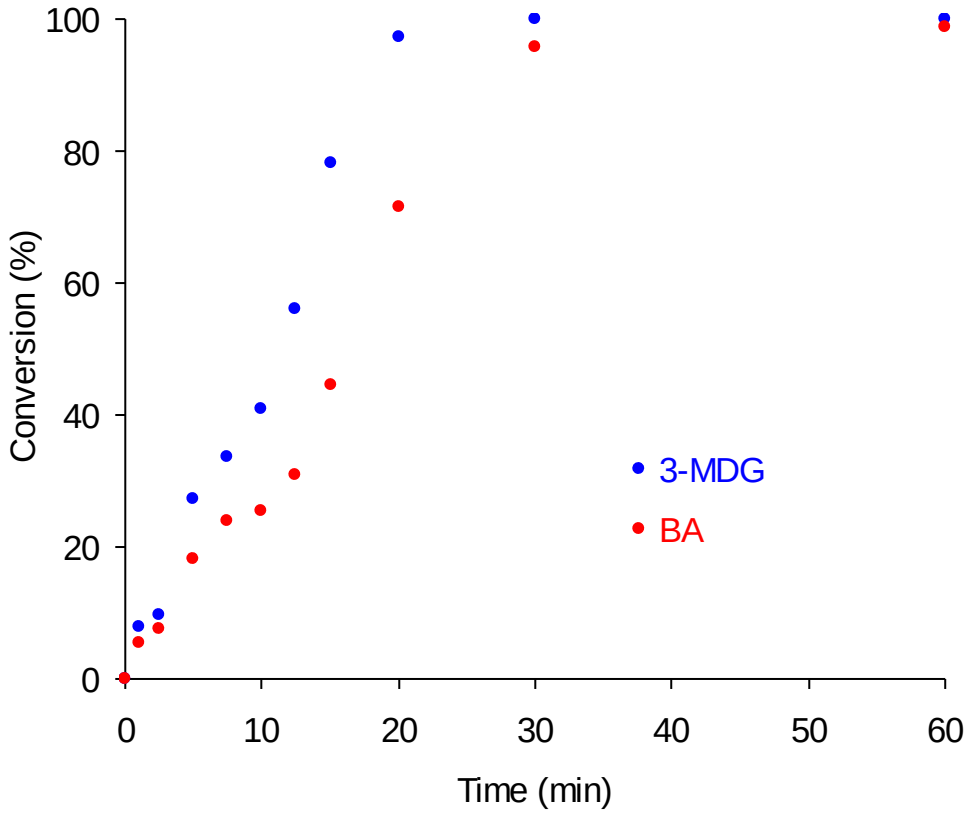


Figure 4.4. Individual conversion of 3-MDG and BA versus time. Polymerization conditions are given in Table 1 with [KPS] of 10.5 mmol/l.

The weight-average molecular weight ($\overline{M}_w$), as gauge to the polymer microstructure, was measured in connection with the initiator concentration. It should be mentioned that emulsion polymerization of (meth)acrylates is combined with crosslinking and chain branching, especially at a high temperature and high conversion. The gel content, amount of insoluble polymer in the solvent, as indicator for the crosslinking and/or branching reactions, was found to be about 50% for BA and BA/MMA polymerization [3-5]. As shown in Table 4.1, the gel content was in the range 60-90% and $\overline{M}_w$ was in the range of 0.9 to 2 × 10^6 g/mol. The high $\overline{M}_w$ could be attributed to the high monomer concentration in the reaction loci. There is an

inverse relationship between the amount of KPS and $\overline{M}_w$. The polydispersity, $\overline{M}_w/\overline{M}_n$, was in the range of 1.5. This value can not precisely predict the termination mechanism because it represents only 10-30% from the total amount of the copolymer.

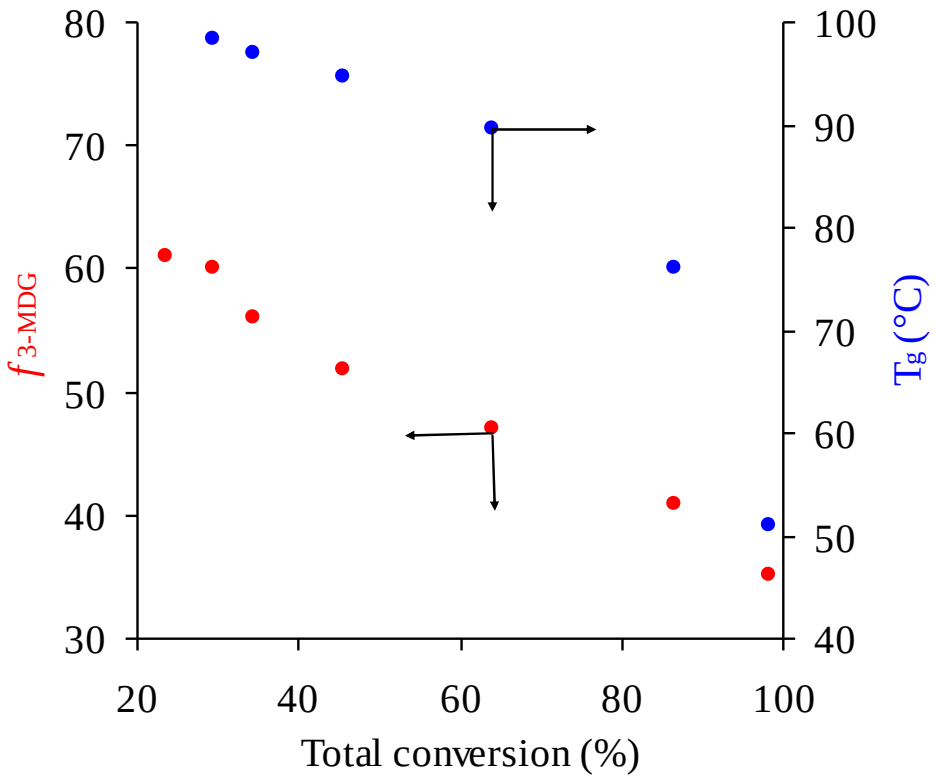


Figure 4.5. Evolution of 3-MDG/BA copolymer composition throughout the polymerization and the influence of the sugar content in the copolymer ($f_{3\text{-MDG}}$) on the glass transition temperature. The polymerization conditions are given in Table 1 with KPS concentration of 10.5 mmol/l.

4.4.2.2 *AIBN as oil-soluble initiator*

The use of an oil-soluble initiator, such as AIBN, in the miniemulsion polymerization has been examined by some authors. Generally oil-soluble initiators are suitable for monomers showing either high water solubility (e.g. MMA) to prevent homogenous nucleation or extremely low water solubility (e.g. lauryl methacrylate, LMA) where the monomer concentration in the water phase is extremely low. The water solubilities of 3-MDG and BA are 2.44 and 2.2 g/l, respectively. These values are relatively high and could enhance homogenous nucleation. As shown in Table 4.1, AIBN concentration was varied from 4.06 to

56.9 mmol/l. In spite of the high particle size (158 nm) at low [AIBN] (4.06 mmol/l), D and therefore N_p were independent of the [AIBN], (Np ∝ [AIBN]$^{-0.01}$, see Fig. 4.6).

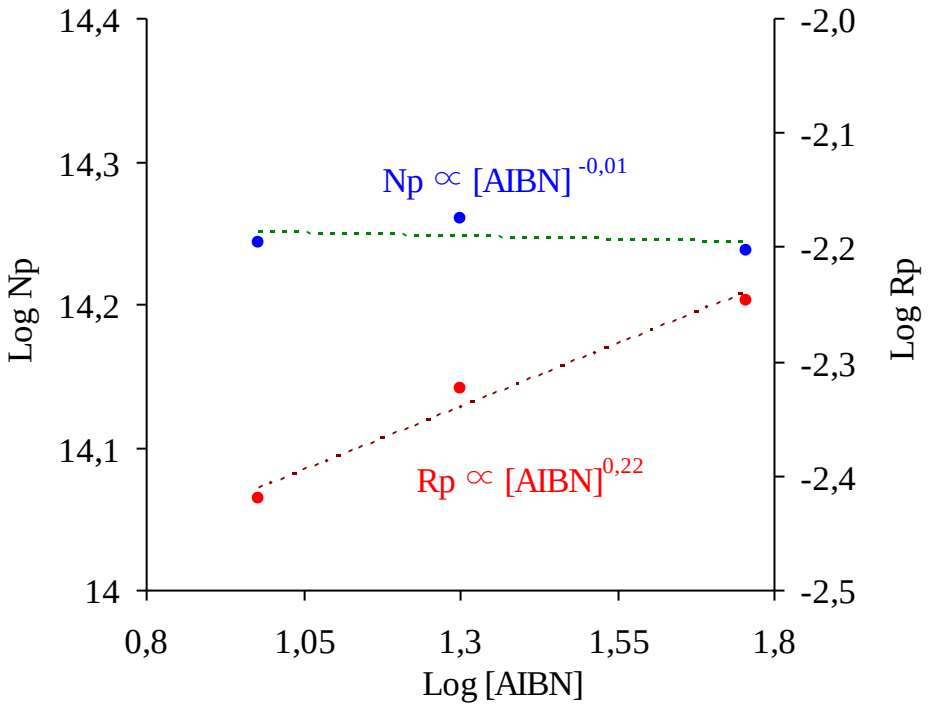
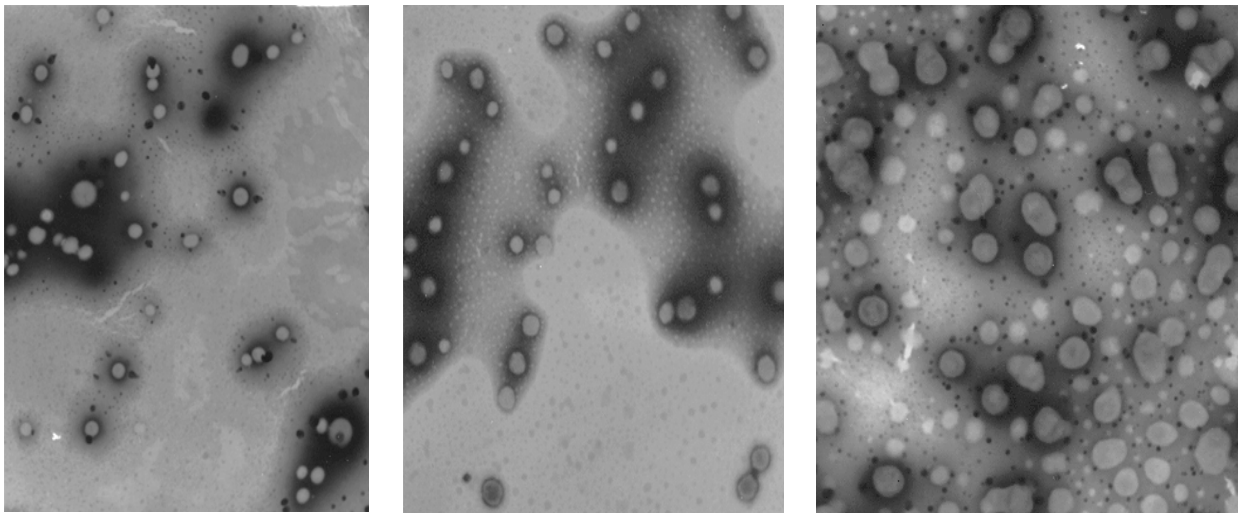


Figure 4.6. Dependence of N_p (•) and R_p (•) on AIBN concentration in miniemulsion copolymerization of 3-MDG/BA at 70 °C. [SDS] was 15.6 mmol/l.

The final latexes exhibit an average *D* value in the range of 130 nm, and an average N_p of 1.75 × 10^{14}/cm^3. The average particle size of the latexes prepared by AIBN was higher than that by KPS (115 nm) under the same polymerization conditions. Chern et al. [6] made comparisons of the initiator type (AIBN vs. KPS) on the extent of homogenous nucleation in styrene miniemulsion polymerization, finding that AIBN promotes the droplets nucleation. On the contrary, the homogeneous nucleation is favored by using KPS. Interestingly, the average *PDI* value of about 0.115, is high and remained unchanged before and after the polymerization. This value rather indicates that sugar latexes prepared by AIBN are polydisperse. The TEM-micrograph of end latex prepared by using AIBN clearly shows the polydispersity of the particles [Fig. 4.7(a)]. Contrary to KPS, R_p is proportional to the 0.22th power of the AIBN concentration (Fig. 4.6). The dependence of N_p and R_p on [AIBN] indicates its affectivity to initiate the monomer droplets and the droplet nucleation could be the dominant mechanism for particle formation. Furthermore, in the case of AIBN, the overall rates of polymerization were twice as low as those carried out by KPS. This can also be ascribed to the smaller particle size in case of KPS in comparison with that by AIBN. The polymerization rate per particle in miniemulsion polymerization in both cases was relatively

similar (R_p/N_p = 1.82 × 10^{-20} mol/sec by AIBN) and (2.12 × 10^{-20} mol/sec by KPS) under similar conditions.



(a) (b) (c)

Figure 4.7. TEM-micrographs of three latexes prepared via miniemulsion polymerization at different conditions: (a) AIBN (19.95 mmol/l) and SDS (15.6 mmol/l); (b) SDS (2.31 mmol/l) and KPS (7.4 mmol/l); and (c) APG (53.5 mmol/l) and KPS (7.4 mmol/l).

As shown in Table 4.1, the gel content was very low (1-4%) in comparison with that formed by KPS. The molecular weights of the polymers prepared by using AIBN were relatively larger than those made by KPS, and they were in the range of 1.7-3.2 × 10^6 g/mol. The high $\overline{M}_w$ could be ascribed to the high monomer concentration in the droplets and the low termination rates. In respect of $\overline{M}_w$ at low [AIBN], it is inversely related to the amount of AIBN and the polydispersity ($\overline{M}_w/\overline{M}_n$) was in the range of 1.5.

The evolution of the number-average molecular weight, $\overline{M}_n$, as a function of conversion by using KPS and AIBN is shown in Figure 4.8. In the case of AIBN, $\overline{M}_n$ shows no dependence on the conversion up to 70 %, but increases sharply above this value and that increase could be related to the gel effect at high conversion. On the contrary, in the case of KPS, $\overline{M}_n$ reaches the maximum value after 20% conversion and gradually decreases after that. This decrease of $\overline{M}_n$ could be related to the enhancement of the crosslinking/branching reactions with the conversion. Fig. 4.9 presents the evolution of the molecular weight distribution during the polymerization. The molecular weight increases significantly at high conversion (X > 60 %) and the molecular weight distribution narrows relatively with the conversion.

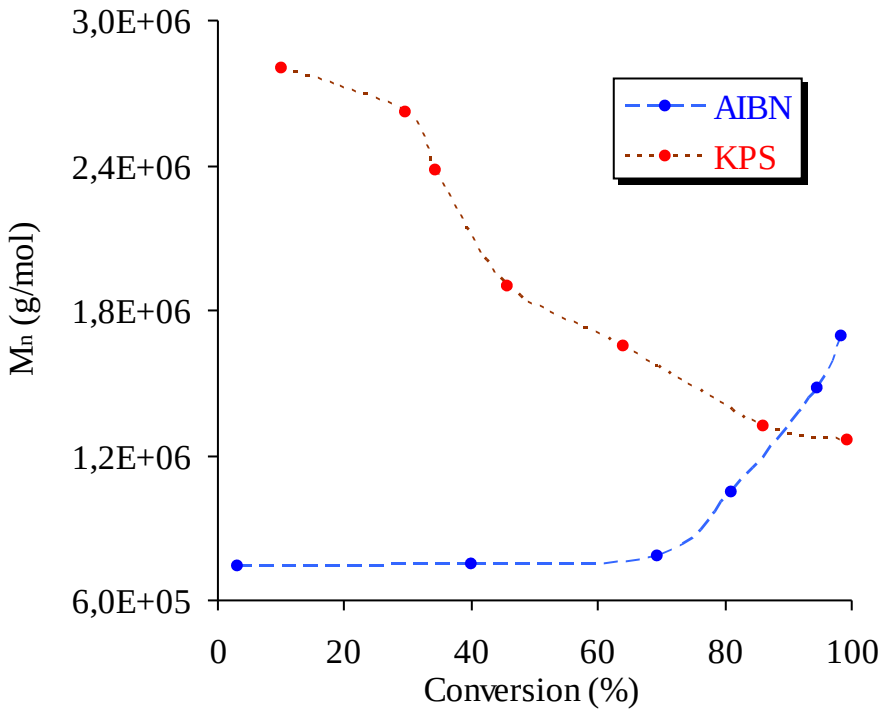


Figure 4.8. Average molecular mass as a function of conversion by using KPS and AIBN as initiators. The polymerization conditions are given in Table 4.1, with KPS conc. of 10.5 mmol/l and AIBN conc. of 56.84 mmol/l.

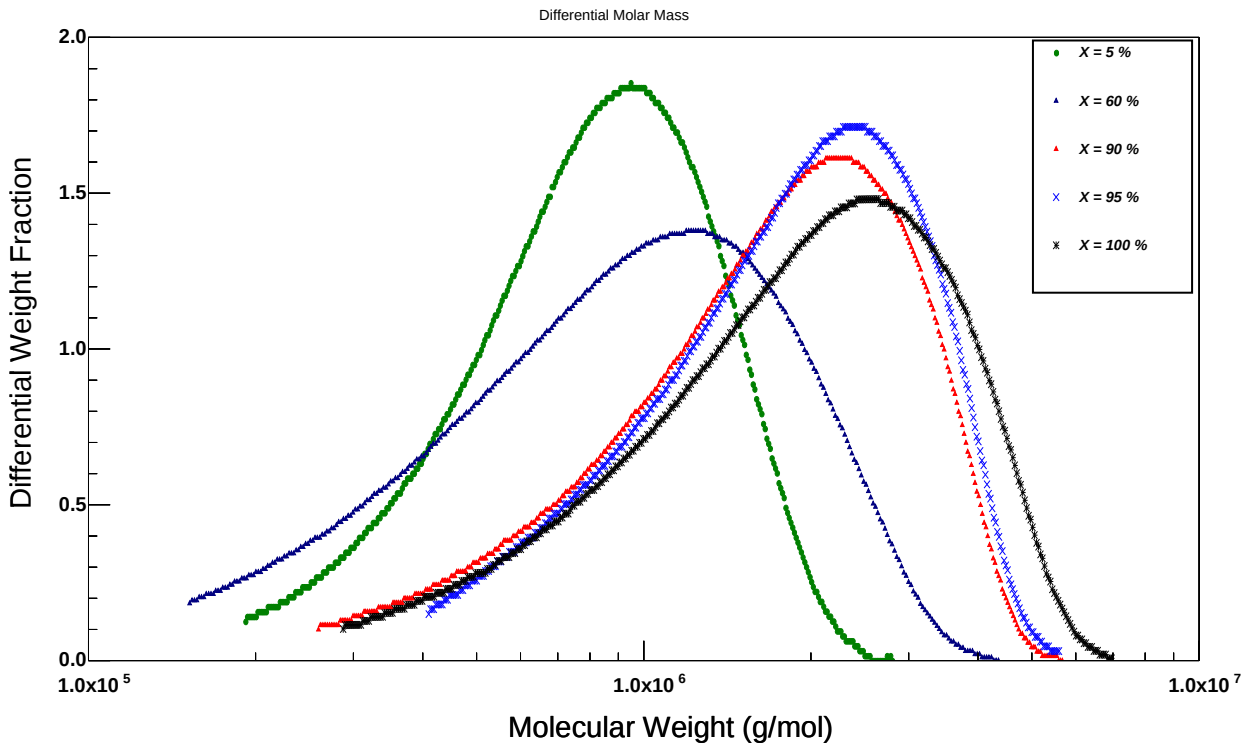


Figure 4.9. Evolution of the molecular weight and its distribution in the miniemulsion copolymerization of 3-MDG/BA by using AIBN as initiator. The polymerization conditions are given in Table 4.1 with [AIBN] = 56.84 mmol/l. *X* donated to the conversion.

Figure 4.10 shows GPC-chromatogram of 3-MDG/BA copolymer prepared in the presence of AIBN as initiator. The copolymer had a high molecular weight of 1.03×10^6 g/mol and low PI of 1.6. The copolymer was completely soluble in THF, which was not the case by the conventional batch emulsion polymerization.

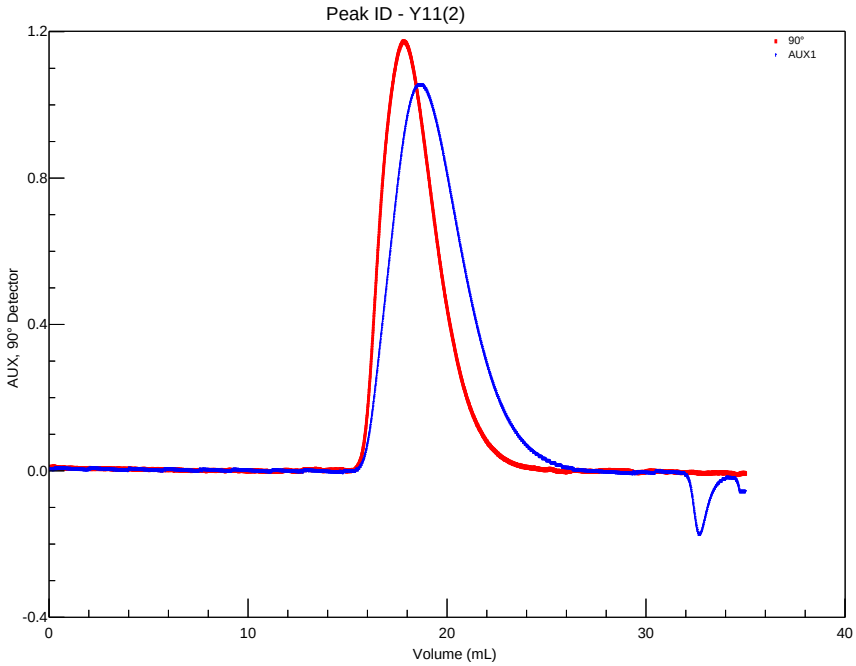


Figure 4.10. GPC-chromatogram of 3-MDG/BA copolymer prepared via free radical miniemulsion polymerization by using AIBN as initiator at 40 % conversion. THF was used as eluent. Red line presents the signal of light scattering detector and blue one of the refractive index detector.

4.4.3 Effect of the type stabilizing systems

4.4.3.1 *SDS/HD stabilizing system*

As we pointed out earlier, miniemulsion droplet size is mainly controlled by the emulsifier concentration. The influence of [SDS] on the reaction kinetics as well as on the polymer colloid features is summarized in Table 4.2. A direct relationship was found between [SDS] and N_p and R_p. Increasing [SDS] from 2.31 to 46.2 mmol/l leads to a decrease in particle size from 179 to 71 nm, which in turn increases N_p and R_p.

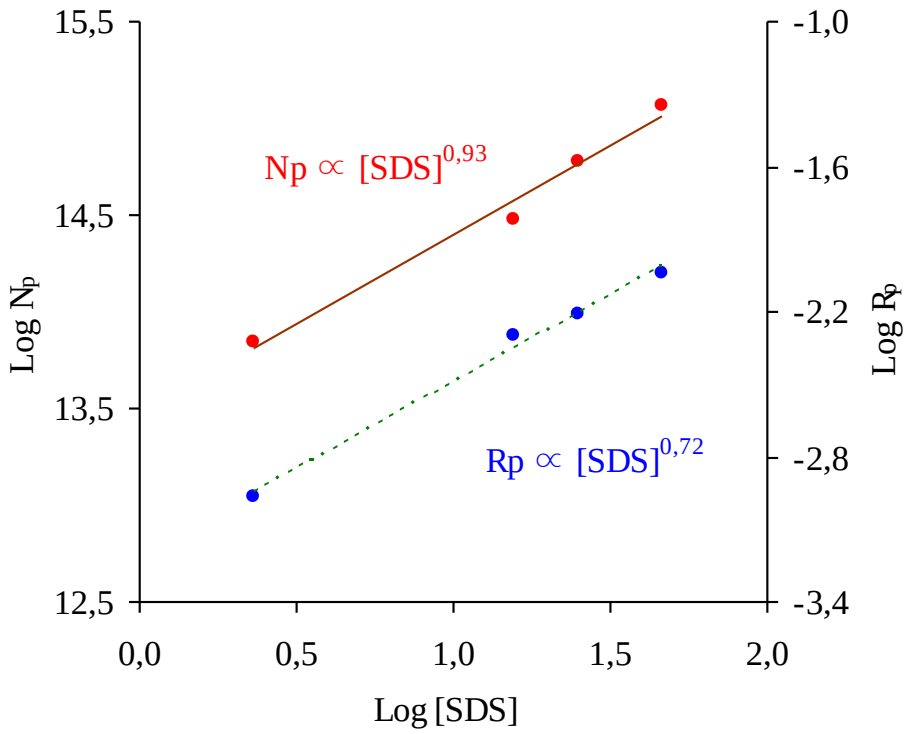


Figure 4.11. Dependence of N_p (•) and R_p (•) on SDS concentration in miniemulsion copolymerization of 3-MDG/BA at 70 °C. [KPS] was 7.4 mmol/l.

As shown in Fig. 4.11, the exponent of the relation $N_p \propto [SDS]^{0.93}$ indicates the affectivity of the emulsifier concentration on N_p. At higher [SDS], more SDS molecules are available to cover the new formed droplets during the homogenizing process. Increasing the reaction loci with the level of SDS enhances the rate of polymerization and shortens the time of polymerization. The exponent (0.72) of the relation $R_p \propto [SDS]^{0.72}$ reflects the range of the dependency of the R_p on [SDS]. This value is quite close to the value (0.56) obtained for the conventional emulsion polymerization of 3-MDG/BA [21]. The *PDI* narrowed with increasing the conversion (about 0.13 before the polymerization and 0.06 after it). This could be due to the small particles polymerizing faster than the bigger ones, which become smaller in size in the course of polymerization due to the monomer diffusion to the growing particles.

The value of $N_{p,f}$ / $N_{p,i}$ increases from 1.2 to 6 (Table 4.2) with increasing [SDS] and this indicates the probability of micellar or homogeneous nucleation occurring beside the droplet nucleation at higher SDS concentration. The increase of *PDI* with increasing [SDS] confirms the previous assumption. Figure 4.7(b) shows TEM-micrograph of sugar latex prepared at a low SDS concentration (2.31 mmol/l). It is evident that the prepared latex is relatively monodisperse.

Table 4.2. Effect of emulsifier type and concentration on the miniemulsion copolymerization of 3-MDG/BA at70°C.

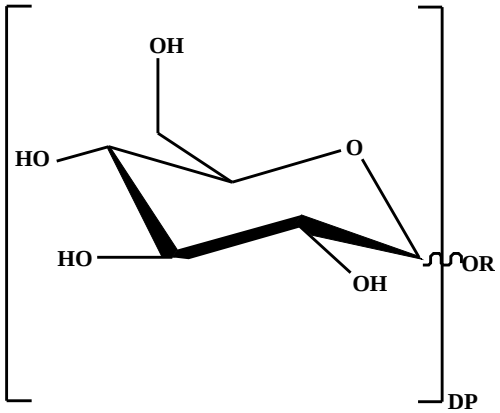
Emulsifier Type / concentration		*D* (nm)	*PDI*	$N_{p,f}$ / $N_{p,i}$	N_p (10^{14}/cm^3)	R_p (10^{-3} mol/L . s)	Final conv. (wt %)	$\overline{M}_w$ (10^6 g/mol)	$\overline{M}_w/\overline{M}_n$	Gel content (wt %)
SDS	(2.31 mmol/l)	179	0.03	1.2	0.69	1.09	98.7	1.79	1.4±0.1	62
	(15.6 mmol/l)	110	0.07	2.0	2.69	5.69	99.6	0.98	1.5±0.2	80
	(25.02 mmol/l)	88	0.09	2.5	6.0	6.20	98.6	1.23	1.5±0.1	87
	(46.2 mmol/l)	71	0.10	6.0	11.6	9.10	99.8	-	-	-
APG	(11.36 mmol/l)	570	0.03	0.1	0.022	0.74	98.3	1.22	1.7±0.2	38
	(16.69 mmol/l)	300	0.05	-	0.147	1.20	99.6	1.31	1.6±0.1	25
	(26.97 mmol/l)	220	0.07	0.65	0.38	2.01	99.9	1.44	1.5±0.1	42
	(53.54 mmol/l)	134	0.13	1.0	1.76	6.59	99.8	1.82	1.4±0.1	19

Reaction conditions: 8.7 g 3-MDG, 6.4 g BA, 0.6 g HD, 0.15 g KPS, 0.03 g $NaHCO_3$, and 60 g of water.

The molecular weight analysis of polymers prepared by using SDS as anionic emulsifier was also difficult as by KPS. The gel content was about 69-90 %. In contrast, by using AIBN as organic initiator or APG as non-ionic emulsifier only about 5-30 % gel content was observed. It was therefore supposed that the ionic emulsifier or initiator enhanced the transfer, branching and crosslinking reactions. The average molecular weight was in the range of 1 to 2 $\times 10^6$ g/mol and the average polydispersity was about 1.5.

4.4.3.*2 APG/HD stabilizing system*

The aim of using APG was the enhancement of the renewable part in the formed latex and to study its behavior as non-ionic emulsifier to stabilize the system 3-MDG/BA. The main character for this system, APG/HD, is the steric stabilization of the monomer droplets. Scheme 4.1 presents the chemical structure of APG, which is prepared from D-glucose or its higher oligosaccharides with long chain fatty alcohol [C_8-C_{16}]. The degree of polymerization (D_p), which represents the average number of glucose units to the alkyl chain, is in the range of 1.2-1.5 [7].



Scheme 4.1 Molecular formula of alkyl polyglucoside (APG)
R = (fatty) alkyl group
Dp = average number of glucose units/alkyl chain (R)

Similar observations were found by APG as well as SDS. As shown in Table 4.2, an increase in [APG] led to a decrease in particle size, and an increase in N_p and enhanced R_p. Fig. 4.12 shows the dependence of N_p, and R_p on [APG]. It is obvious that N_p strongly depends on APG concentration. An exponent value of 2.22 was obtained for the total number of particles of the end latex versus [APG]. A linear relationship between the R_p and [APG] was also found with an exponent value of 1.4. The rate of polymerization in the presence of SDS was three times faster than those conducted by using APG, at the same emulsifier concentration. This could be ascribed to the smaller particle size in case of SDS in comparison to APG.

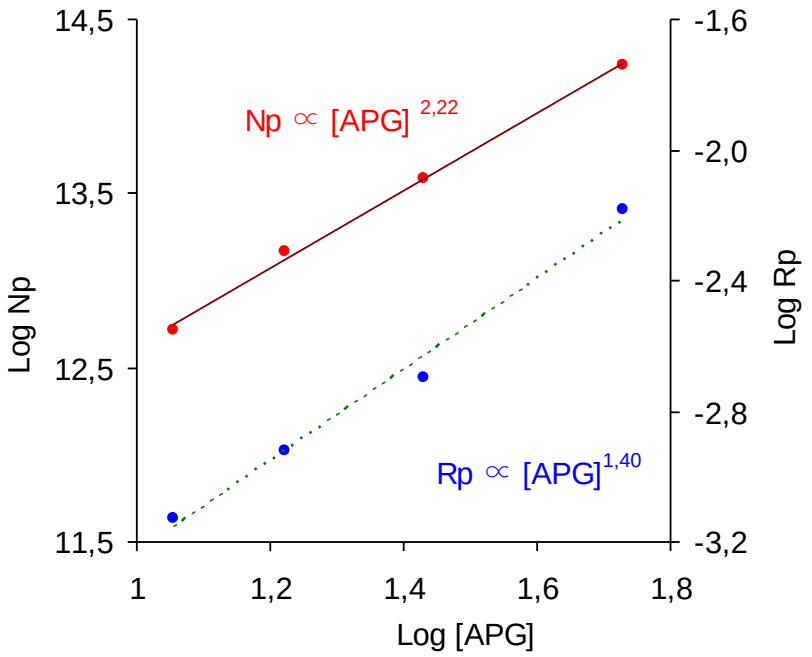


Figure 4.12. Dependence of N_p (•) and R_p (•) on APG concentration in miniemulsion copolymerization of 3-MDG/BA at 70 °C. [KPS] was 7.4 mmol/l.

For example, the particle size of the end latex prepared by SDS was 220 nm at 27 mmol/l of APG, with SDS it was 88 nm at a concentration of 25 mmol /l. It may also be related to the steric hindrance of the macroradical entry to the monomer droplets in case of APG. Contrary to the case of SDS, the $N_{p,f}/N_{p,i}$ ratio at low APG concentration is very low (0.1).

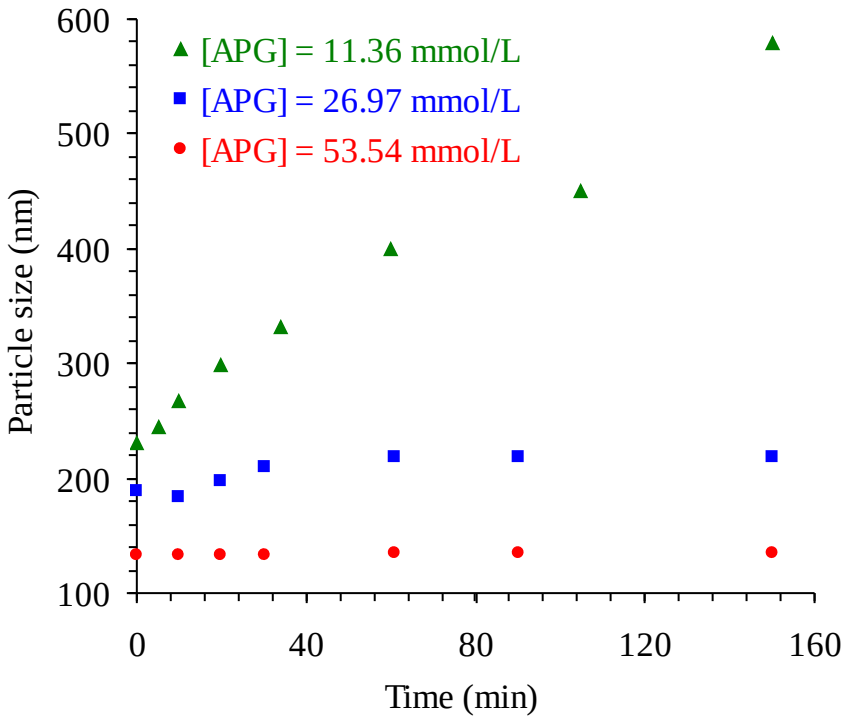


Figure 4.13. Particle size versus time for miniemulsion copolymerization of 3-MDG/BA at different APG concentrations with [KPS] of 7.4 mmol/l.

Fig. 4.13 clearly shows that at low [APG], the particle size steadily increases during polymerization. This strong increase in the particle size can be related to a coagulation process at low conc. of APG. At higher APG concentration the $N_{p,f}/N_{p,i}$ ratio is equal to unity, which confirms full droplet nucleation. The values of *PDI* show that monodisperse latex at low APG, and polydisperse one at high [APG] were prepared. The *PDI* widens with enhancing the emulsifier concentration, which probably indicates that a micellar and/or homogeneous nucleation occurs besides the monomer droplet nucleation.

Fig. 4.7(c) shows TEM-micrograph of end latex prepared by using APG (53 mmol/l). The latex is polydisperse and some particles coalesced together, which could be due to a chemical interaction, such as hydrogen bonding, between the hydroxyl groups of the glucose moieties of APG.

The molecular weight was in the range of 1.2 to 1.8 x 10^6 g/mol. The increase of $\overline{M}_w$ with [APG] could be related to the decrease of the particle size and consequently reducing the chain radical termination by combination. The increase of [APG] narrowed the molecular weight distributions. Furthermore, the gel content in the case of nonionic emulsifier is lower than that by an anionic one. Fig. 4.14 shows the evolution of the molecular weight and its distribution at different APG concentration. This again shows that at high APG concentration, the nucleation of monomer droplets is the more probable nucleation mechanism.

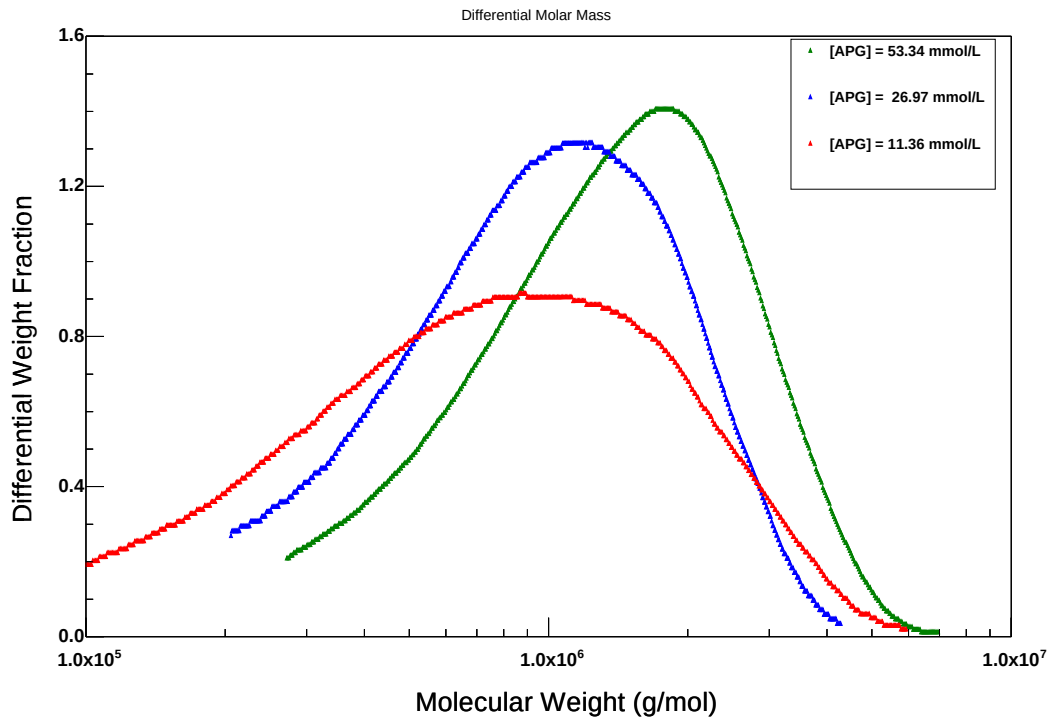


Figure 4.14. Evolution of the molecular weight and its distribution in the miniemulsion copolymerization of 3-MDG/BA by using APG with different concentrations. The polymerization conditions are given in Table 4.2.

4.5 CONCLUSIONS

Synthesis and characterization of saccharidic polymer colloids via free radical miniemulsion copolymerization of 3-MDG/BA were investigated. The influence of some reaction parameters such as the emulsifier and the initiator on the colloidal features (the particle size and the particle size distribution) was shown. A tailor made sugar latex can be obtained by adjusting the formulation ratios (monomers/costabilizer /emulsifier/initiator/water/etc.). It was found that the type and the concentration of the initiator did not affect the particle size of the end latex. In the range of the studied KPS and AIBN concentrations, a 1:1 droplets/polymer particles copy process is obtained. Finally, when the emulsifier (anionic or nonionic) concentration increased, the particle size decreased, and consequently the overall polymerization rate increased. In the investigated range of SDS and APG concentrations, a 1:1 copy process is only achieved at a low SDS and a high APG concentration. The increasing of KPS or AIBN concentration enhanced R_p. Latex polymers prepared by using ionic emulsifier or ionic initiator or both together contain more gel (branched or crosslinked polymers) than those prepared by nonionic emulsifier or organic initiator or both together.

4.6 REFERENCES

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Chapter 5

Synthesis of Well-designed Polymers Bearing-Saccharide Moiety via Living Radical Miniemulsion Polymerization by using Reversible Addition-Fragmentation Chain Transfer (RAFT) Technique

5.1 ABSTRACT:

Well designed polymer latexes bearing saccharides based on 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG) and, 3-*O*-methacryloyl-1,2:4,5-di-*O*-isopropylidene-α-D- fructopyranose (3-MDF), were prepared via reversible addition-fragmentation transfer (RAFT) in miniemulsion. Three different RAFT agents, i.e. 1-phenylethyl dithiobenzoate (PED), 2-phenylprop-2-yl dithiobenzoate (PPD), and 2-cyanoprop-2-yl dithiobenzoate (CPD), were used to control the polymerization and the growth of the living chains. With PED, no living character was found and the final polymers exhibit a polydispersity index (PI) around 1.7. In the presence of CPD, a poly(3-MDG) with PI of about 1.5 was obtained. In contrary, PPD has proven as very suitable agent to 3-MDG polymerization and the formed polymer has a PI lower than 1.2. The rate of RAFT miniemulsion polymerization of 3-MDG was relatively lower in comparison with the conventional miniemulsion polymerization under the same conditions. The preparation of poly(3-MDG) in miniemulsion with a PI of 1.05 and $\overline{M}_n$ in the range of $5x10^4$ g/mol in a short reaction time of 100 min was successfully realized. Furthermore, poly(3-MDG) was also extended with other monomers such as alkyl (meth)acrylates yielding various block copolymers containing 3-MDG and butyl or methyl methacrylate.

Keywords: miniemulsion polymerization, polymer bearing saccharide, block copolymer, reversible addition-fragmentation transfer (RAFT), latex.

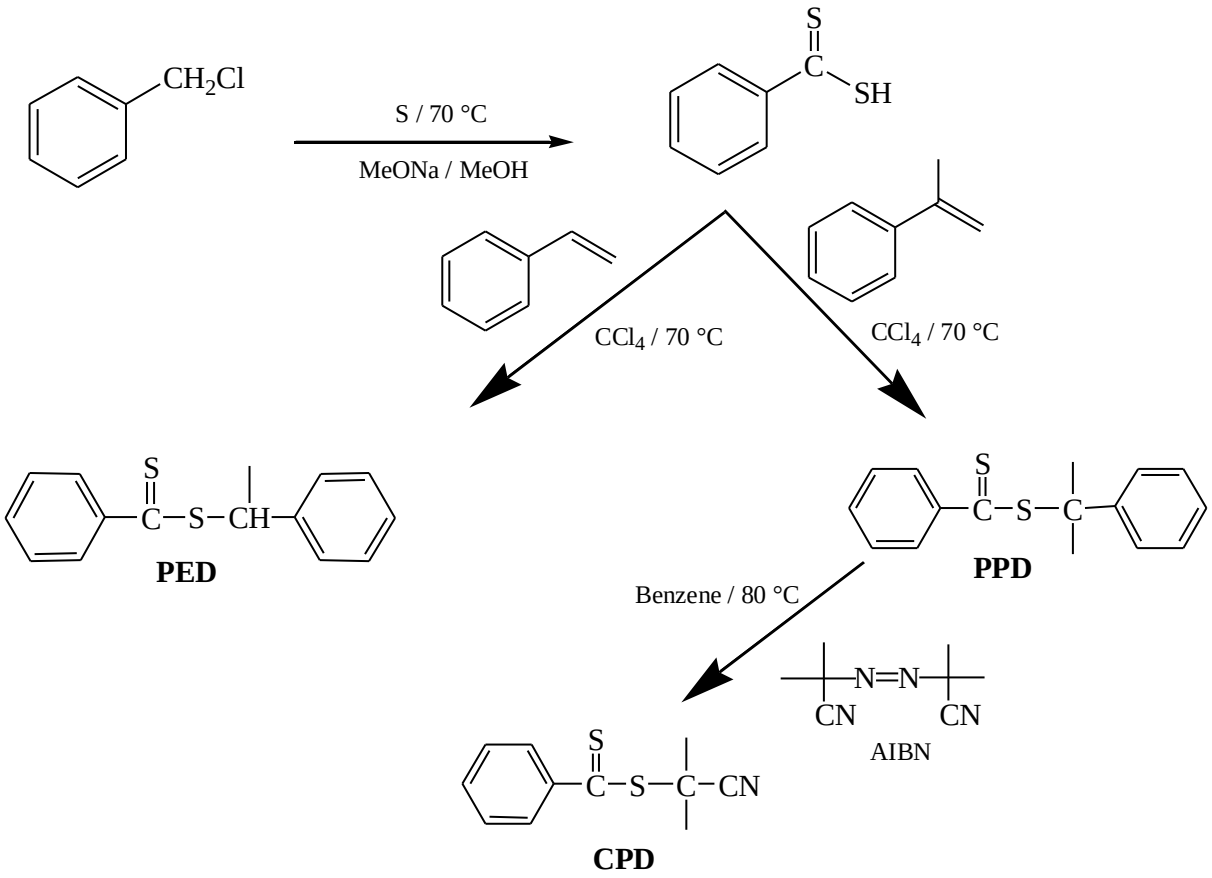
5.2 Introduction

We have given in chapter 1.4 a brief introduction on the living/controlled free radical polymerization and its application to heterogeneous systems. Most of the controlled living polymerizations concerning few vinyl sugar monomers were carried out either in mass or in solution [1-12]. Miniemulsion polymerization as a new and interesting technique is rapidly becoming a useful tool in the synthesis of complex polymer architectures.

The aim of this study is the use of reversible addition-fragmentation transfer (RAFT) technique in miniemulsion polymerization to prepare polymer colloids containing sugar moieties. We have already reported in the previous chapter on the miniemulsion polymerization of 3-MDG/BA. Although latexes were obtained with interesting properties, the resulting copolymers structure is random. The second aim of this study is the synthesis of block copolymers containing a sugar derivative as one long segment. The partially hydrolysis of the sugar moieties is conducted to functionalize the latexes with hydrophilic saccharide blocks, having hydroxyl groups at the outer shell of the particles.

RAFT process is applicable to a wide range of monomers (most polymerizable monomers by free radical method). However, there is no universal RAFT agent suitable for all monomers. Reactive monomers such as alkyl methacrylates, with high propagation rate constants, need RAFT agents with high activity. For example, for MMA only two RAFT agents (PPD and CPD) from more than 10 agents were capable to produce polymer with living character, i.e. low molecular weight and possible extension of the polymer chains [13].

Three RAFT agents with different structures and reactivities were synthesized and tested in order to found the appropriate one for 3-MDG and 3-MDF (scheme 5.1 and appendix 5, p. 157-160). These RAFT agents are 1-phenylethyl dithiobenzoate (PED), 2-phenylprop-2-yl dithiobenzoate (PPD), and 2-cyanoprop-2-yl dithiobenzoate (CPD). They were used to obtain poly(3-MDG) or poly(3-MDF) with low molecular weight distribution and ability to extent it with other block monomers such as alkyl (meth)acrylates. The difference between these agents is in the reactive group or the leaving group (R). These RAFT agents were investigated in polymerization of MMA, analog to 3-MDG, in bulk and solution at 60 °C [13]. The authors reported that the apparent chain transfer constant (C_{tr}) is 0.16, 10, and 13 for PED, PPD, and CPD, respectively. According to the requirement for good living polymerization, C_{tr} should be greater than 2.



Scheme 5.1. Chemical preparation of three RAFT agents: 1-phenylethyl dithiobenzoate (PED), 2-phenylprop-2-yl dithiobenzoate (PPD), and 2-cyanoprop-2-yl dithiobenzoate (CPD).

More attention was taken by the preparation of 3-MDG miniemulsion because stable miniemulsion, at least during the course of polymerization, is essential to achieve well living character. From the previous results in miniemulsion polymerization (chapter 4), it was found that low anionic emulsifier concentration is essential to prevent the micellar nucleation, which can occur simultaneously with the droplets nucleation. Anionic emulsifier (SDS) was used for stabilization the miniemulsion and there was no stability problems as observed by Monteiro et al. [2, 3] when using SDS as an emulsifier for stabilization of (meth)acrylates miniemulsion. Long sonication time (10 min) was used to ensure full homogenizing of the miniemulsion. The polymerization was initiated directly as soon as the miniemulsion reached the polymerization temperature.

5.3 EXPERIMENTAL

5.3.1 Materials

The sugar monomers, 3-MDG and 3-MDF, were prepared as described before [26-33 in chapter 1]. The comonomers BMA, MMA and BA (Fluka) were distilled just before use. Sodium dodecyl sulfate (SDS, Merck) was used as an anionic emulsifier. Hexadecane (HD, Aldrich) was used as hydrophobic costabilizer. All other ingredients were used as received. Potassium persulfate (KPS, Merck) and sodium bicarbonate ($NaHCO_3$, Merck) were used as initiator and buffer, respectively. The oil-soluble initiator 2,2´-Azobisisobutyronitrile (AIBN, Fluka) was used without any purification. Three RAFT agents, 1-phenylethyl dithiobenzoate (PED), 2-phenylprop-2-yl dithiobenzoate (PPD), and 2-cyanoprop-2-yl dithiobenzoate (CPD), were synthesized as described in the literature [13] (see appendix 5).

5.3.2 RAFT- Miniemulsion polymerization of 3-MDG

Preparation of the miniemulsion: The finely powder 3-MDG monomer was mixed with HD and RAFT agent and heated between 40-50 °C to melt the sugar monomer. This oily phase was then added to an aqueous solution containing the required amount of SDS and $NaHCO_3$. The mixture was stirred for 20 min at 40 °C under argon atmosphere. The mixture is subjected to very high shear by ultrasonication for 10 min at 60 % amplitude with a "*Sonopuls*" homogenizer HD 2200 (from BANDELIN). By using AIBN, it was mixed firstly with the oil phase. By using KPS, the aqueous solution of KPS was added after the homogenization and just prior the polymerization.

Polymerization procedure: The polymerization was carried out at 70 °C in 200 ml double wall glass reactor equipped with a glass stirrer, a reflux condenser, nitrogen inlet, and sample device. The polymerization was started, directly, by the addition of the initiator solution after the miniemulsion attained the polymerization temperature. The polymerization was monitored by withdrawing samples from the reactor during the polymerization.

5.3.3 Block copolymerization by RAFT-miniemulsion polymerization of 3-MDG and alkyl (meth)acrylates

The block copolymerization was carried out in two successively steps: i) The first step as already mentioned above, ii) the second step is directly realized by an addition of another monomer and was conducted by the sequential addition technique. In this case the polymer colloids formed in the first step could be considered as seed latex for the second step. The comonomer was added to the seed latex, directly, after the consumption of the monomer in the first step.

5.3.4 Characterization of the Latexes

The rate of polymerization and the characterization of the latex properties such as the particle size and its distribution were investigated. The block copolymer composition was performed by ^{1}H NMR and T_g measurements as described in the previous chapters (2-4).

5.3.5 Molecular Weights

The weight-average molecular weight ($\overline{M}_w$) was determined by gel permeation chromatography (GPC) online with a multi-angle laser light scattering (MALLS) and refractive index (RI) detector. Then the number-average molecular weight ($\overline{M}_n$) was estimated. Polymers solutions in tetrahydrofuran (THF), about 5-8 g/l, were analyzed at 25 °C using two columns (Plgel MIXED-C, particle size 10µm, length/I.D. 300 ×7.5 mm). The separation range of the columns is from 500 to 10^6 g/mol. THF was used as eluent with a flow rate of 1 ml/min. The refractive index increment, *dn/dc*, of poly(3-MDG) is 0.0735. It was measured on a light-scattering photometer at 25 °C in THF, and at a wave length of 633 nm [8]. The light scattering detector (MALLS) was calibrated by using a filtered pure toluene (HPLC-grade). Monodisperse poly(styrene) standard with $\overline{M}_n$ of 28500 g/ mol and PI < 1.05 was used to: (a) determine the MALLS-RI volume delay; (b) determine the instrument's normalization coefficients; (c) check the RI calibration constant; and (d) check the MALLS calibration constant.

The theoretical number-average molecular weight ($\overline{M}_n$) was calculated as described by the equation 8 in chapter 1.4 (p.47).

5.4 RESULTS AND DISCUSSION

5.4.1 RAFT polymerization with 1-phenylethyl dithiobenzoate (PED)

PED was used as RAFT agent in bulk polymerization of MMA at 60 °C yielded a polymer with a PI of 1.9. The low chain transfer constant of PED to MMA (0.16) proves that PED is an unsuitable agent for controlling the growth of MMA living chains. Contrarily, by solution polymerization of BA at 60°C in benzene, PED gives polymer with a low PI in the range of 1.13 [13]. The unsuccessful results of living radical polymerization of MMA by using of PED may indicate that this agent will not give a good result in the polymerization of 3-MDG, since 3-MDG and MMA have a similar propagation rate constants (k_p of 3-MDG, MMA and BMA at 70°C are 1265, 900 and 1220 L .mol^{-1}.s^{-1} respectively).

Table 5.1 shows the polymerization conditions and the results of RAFT-miniemulsion polymerization of 3-MDG and BMA by using PED at 70 °C. From these results, the following main points can be extracted: I) the increase of PED concentration leads to a retardation in the rate of polymerization, II) the average-number molecular weight ($\overline{M}_{n,Exp}$) is about 20 times bigger than the theoretical value ($\overline{M}_{n,Th}$), III) the polymerization proceeded in an uncontrolled manner, and IV) the average polydispersity of the end polymer is in the range of 1.6-1.8.

Table 5.1. Recipe and results of RAFT-miniemulsion polymerization of 3-MDG and BMA with PED.

EXP.[a)]	Monomer	PED (g)	PED (%)[c]	Conv. (%)	Time (min)	$\overline{M}_{n,Th}$ x10^{-4} g/mol	$\overline{M}_{n,Exp}$ x10^{-4} g/mol	PI
R1	3-MDG	0.045	0.30	90	30	8.12	103	1.54[d]
R4	3-MDG	0.32	2.09	82	60	1.14	25.1	1.82
R6	3-MDG	0.400	2.60	94	60	1.19	21.27	1.90
R11[b]	3-MDG	0.400	2.60	60	150	0.49	31.3	1.58
R10	BMA	0.479	3.09	35	120	0.81	9.01	1.59

a) The amounts of monomer 15 g, water 135 g, SDS 0.24 g, HD 0.5 g, KPS 0.08 g (0.53% based on monomer), and $NaHCO_3$ 0.1 g were hold constant for all the runs.
b) AIBN was used as initiator, 0.08 g.
c) based on the monomer.
d) The sample was not completely soluble in THF.

Figure 5.1 shows the conversion-time curve for RAFT-miniemulsion polymerization of 3-MDG at different PED concentrations. The effect of PED concentration on the conversion is insignificant at low conversion (<20%). The rate of polymerization decreased relatively by increasing [PED]. For the run R11, by using AIBN as initiator, the retardation was also observed and was more pronounced. Only 60% conversion was obtained after 150 min. The high PED concentration and the low efficiency of AIBN could be the reason of this retardation.

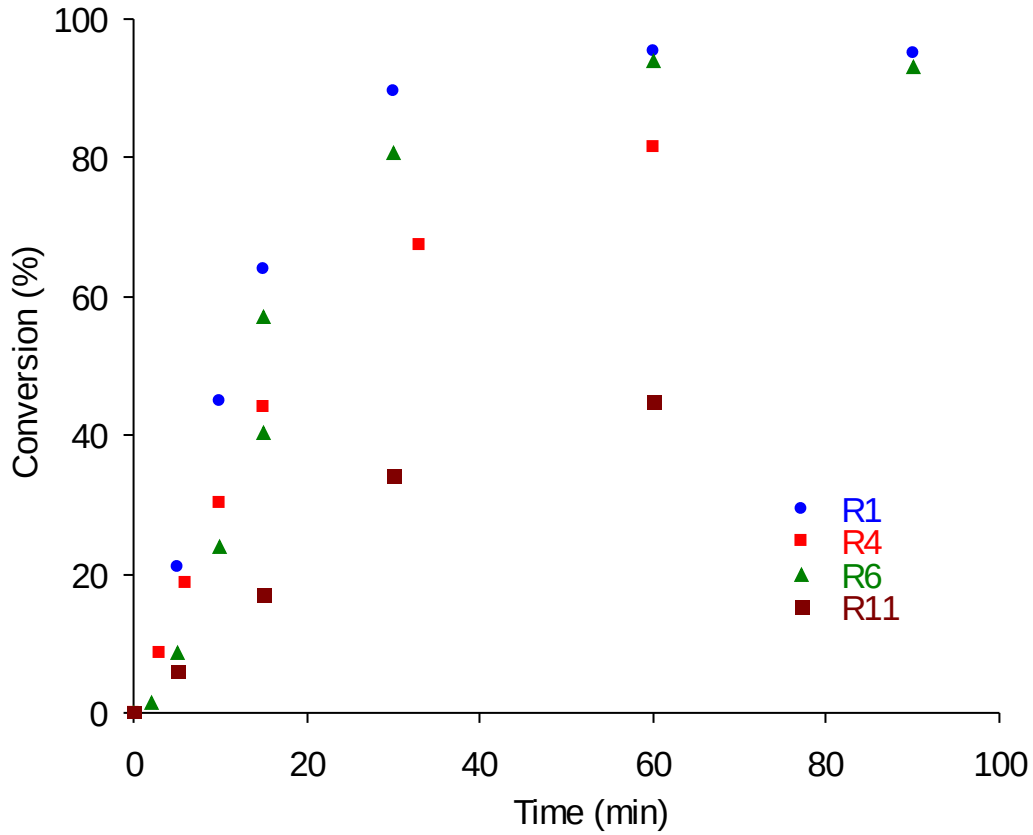


Figure 5.1. Influence of the initial PED concentration on the evolution of monomer conversion as a function of reaction time.

The particle size of the final 3-MDG latex was in the range of 190-210 nm and the PDI (D_w/D_n) was in the range of 0.1. The miniemulsion shows a good stability during the course of polymerization. In case of BMA miniemulsion polymerization (R10), the particle size was significantly lower (110 nm) with a PDI of 0.1.

Furthermore, the molecular weight of polymers did not increase with the conversion and the polydispersity index during the polymerization was in the range of 1.7 (Figure 5.2). The number-average molecular weight had an average value of about 2.5×10^5 g/mol and this value slightly decreased at the end of polymerization (over 80% conversion). These poor results could be related to the low transfer coefficient of PED to methacrylate monomers. The

apparent chain transfer constant of PED to 3-MDG was calculated on the run R6 as described in literature [13] and it was found to be 0.87 (Figure 5.3). This value is relatively higher than that found in case of MMA at 60 °C. Generally, the molecular weight of polymers made by PED was about 10 times lower than that made without this agent. Furthermore, most of polymer samples, prepared by PED, were soluble in THF (no gel polymer or crosslinked polymer).

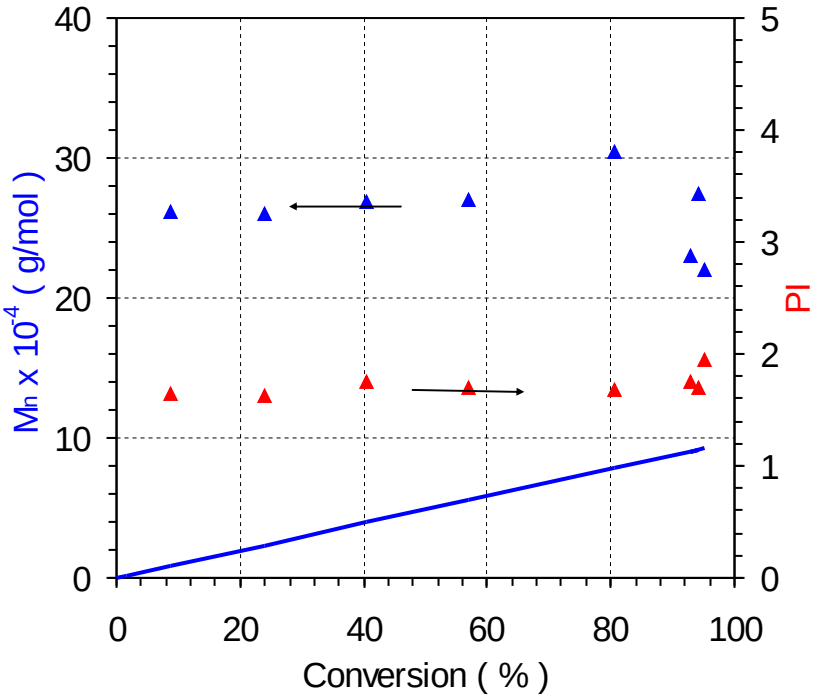


Figure 5.2. Evolution of $\overline{M}_n$ (▲) and PI (▲) as a function of conversion for 3-MDG miniemulsion polymerization at 70 °C with PED, run R6. The straight line represents the conversion evolution of the theoretical $\overline{M}_n$.

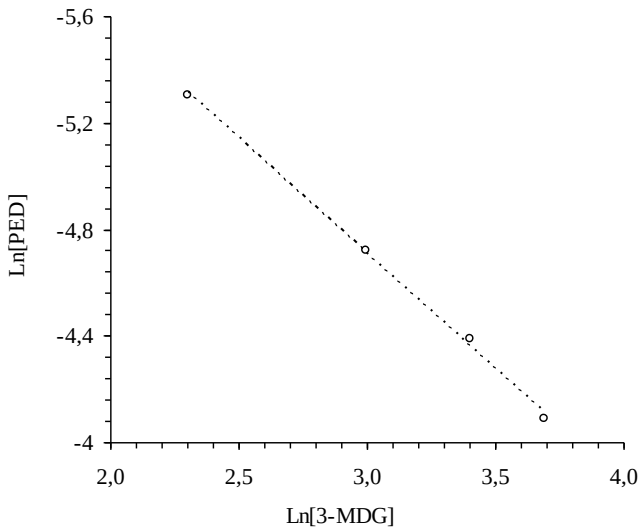


Figure 5.3. Double log plots of PED concentration versus 3-MDG concentration for the run R6. The polymerization conditions are given in Table 5.1.

In spite of the poor results of PED in the polymerization of 3-MDG, we have tried to built a block copolymer with BA, MMA, and BMA. As shown in Table 5.2, over 80% conversion was obtained for the second polymerization step in 180 min. Surprisingly there is no increase in $\overline{M}_n$ and PI widen relatively to about 2.

Table 5.2. Recipes and results of block copolymerization of 3-MDG, BMA and BA in miniemulsion. PED was used as RAFT agent for the preparation of seed latexes in the first step.

EXP.	Seed Type	(g)	Comonomer Type	amount (g)	KPS (g)	Conv. (%)	$\overline{M}_{n,Th}$ x10^{-4} g/mol	$\overline{M}_{n,Exp}$ x10^{-4} g/mol	PI
R7	R6	75	BMA	7.5	0.05	98	1.68	21.57	1.92
R4´	R4	135	BA	4.86	0.05	80	1.56	24.6	1.83
R9	R6	33.5	MMA	5.61	0.05	78	2.41	22.5	1.71
R10´	R10	27.8	3-MDG	2.4	0.03	97	1.02	37.98	1.78
R11´	R11	80.2	BMA	7.63	0.05	78	1.53	11.47	2.36

The seed R6 has D = 162 nm, PDI = 0.086, and 95% end conversion.

The copolymer of run R7, poly(3-MDG/BMA), shows two distinct T_g values of 26.6 and 158.1 °C, which represent the T_g of each polymer sequence of BMA and 3-MDG, respectively (Figure 5.4). The molecular weights of copolymers at the end of the second step remained unchanged ($\overline{M}_n$ = 2.5 x 10^5; PI ≈1.8). This means that the formed copolymer is not really block copolymer.

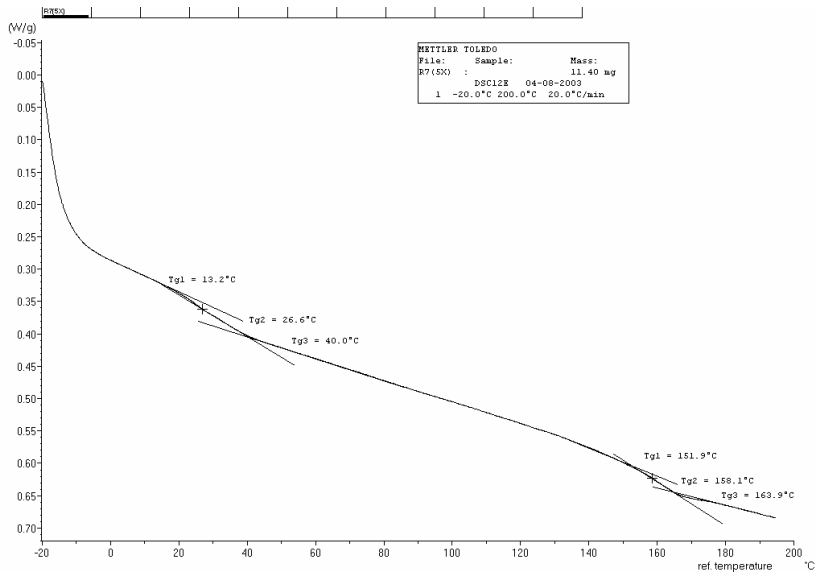


Figure 5.4. DSC-curve showing two different transition states of copolymer R7.

5.4.2 RAFT polymerization with 2-phenylprop-2-yl dithiobenzoate (PPD)

Cumyl dithiobenzoate or 2-phenylprop-2-yl dithiobenzoate (PPD) was used as RAFT agent for a wide range of monomers. Moad et al. reported on the use of PPD in polymerization of BA, MMA, and styrene [16]. They found a significant retardation in the rate of polymerization in case of solution polymerization of BA in MEK (50 % w/w) at 80 °C. Nevertheless, poly(BA) with a low PI of 1.2 and $\overline{M}_n$ of 3.4 x 10^4 g/mol at low [PPD] was synthesized. MMA was polymerized in bulk and solution in the presence of PPD [13]. Poly(MMA) having PI of 1.1-1.2 and $\overline{M}_n$ of 5.6 x 10^4 g/mol was formed. Also, narrow molecular weight distribution of poly(St) was obtained (PI = 1.2) with an average $\overline{M}_n$ of 1.9x10^4 g/mol. Nevertheless, the conventional emulsion polymerization of St and MMA in the presence of PPD yielded polymers with a PI of 7.09 and 1.54, respectively. This was related to the heterogeneous nature of the system and to the inhomogeneous distribution of PPD between the reaction loci due to its low water solubility. Miniemulsion polymerization of St was conducted at 75 °C in the presence of PPD. Low conversion of 35%, was found in 6 h and the formed polymer had a PI of 2.2 and $\overline{M}_n$ of 7x10^3 g/mol. Contrarily, miniemulsion polymerization of methacrylate derivatives in the presence of PPD led to polymer with a low PI of 1.1-1.2. From these studies, we can assume that;

I) PPD is a suitable RAFT agent for a wide range of monomers.

II) the affectivity of PPD as control agent depends on the polymerization process,

III) PPD gives good results in bulk, solution and miniemulsion polymerization for alkyl methacrylates, and poor results in conventional emulsion polymerization.

RAFT-miniemulsion polymerizations of 3-MDG and 3-MDF were investigated at different PPD concentrations (Table 5.3). The preparation of new block copolymers such as poly(3-MDG-*b*-BMA) and poly(3-MDF-*b*-BMA) were conducted by using a sugar seed latex, which was prepared in the first step by using PPD as RAFT agent. In the second step, BMA was added to the seed latex as batch-wise. The SDS/HD stabilization system was used and showed a good stability during entire the polymerization.

As shown in Table 5.3, runs R20, R22, R23, and R28 were carried out under the same conditions by using different PPD concentrations. R22 was conducted in the absence of PPD as a control reaction. R30 was conducted on 3-MDF, a D-fructose based monomer, under the same conditions as for R23.

Table 5.3. RAFT-miniemulsion polymerization of 3-MDG with **PPD** (first step) and block copolymerization with different comonomers (second step), both at 70 °C.

Exp.[a]	Monomer		Mass seed (g)	RAFT **PPD** (g)	Conv. (%)	Time (min)	D (nm)	$\overline{M}_{n,Th}$ x10^{-4} (g/mol)	$\overline{M}_{n,Exp}$ x10^{-4} (g/mol)	PI
	type	amount (g)								
R20	3-MDG	15.0	--	0.4	99	150	233	1.05	2.77	1.01
R22	3-MDG	15.0	--	--	99	60	186	--	--	--
R23	3-MDG	15.0	--	0.23	95	120	242	1.73	3.60	1.2
R28	3-MDG	15.0	-	0.11	95	120	216	3.49	6.91	1.62
R30	3-MDF	15.0	--	0.23	91	220	284	1.66	4.12	1.25
Exp. [b]	Comonomer			**KPS** (g)						
	type	amount								
R21	BMA	8.77	81.6	0.1	94	240	262	2.10	3.71	1.10
R24	BMA	6.0	60.0	0.1	60	300	252	2.82	5.62	1.32
R28´	BA	7.51	119.0	0.1	45	180	262	4.49	13.16	1.98
R30´	BMA	10.9	123.0	0.1	87	150	350	2.95	8.44	1.18
R30´´	BA	11.12	135.0	0.1	17	150	350	3.20	9.16	1.31

a) Reaction conditions of the first step: The amounts of water (135 g), SDS (0.24 g), HD (80.5 g), KPS (0.08 g), and $NaHCO_3$ (0.1 g) were hold constant for all the runs.

b) Conditions for block copolymerization in the second step: 0.1g of KPS was dissolved in 3 ml water and was added to the seed latex after the addition of the comonomer.

Figure 5.5 shows the conversion-time curve at different concentrations of PPD. Without PPD, R22 takes place under the radical miniemulsion polymerization conditions and exhibits the higher R_p. The increase of [PPD] retarded the rate of polymerization. This is an indication to the participation of PPD in the polymerization mechanism. The polymerization of 3-MDF in the presence of PPD (R30), proceeded more slowly than that by 3-MDG (R23) due to their different structures. The steric hindrance around the polymerizable double bond at C-3 of the pyranoid ring for 3-MDF could be markedly higher than the C-3 position of 3-MDG furanoid ring.

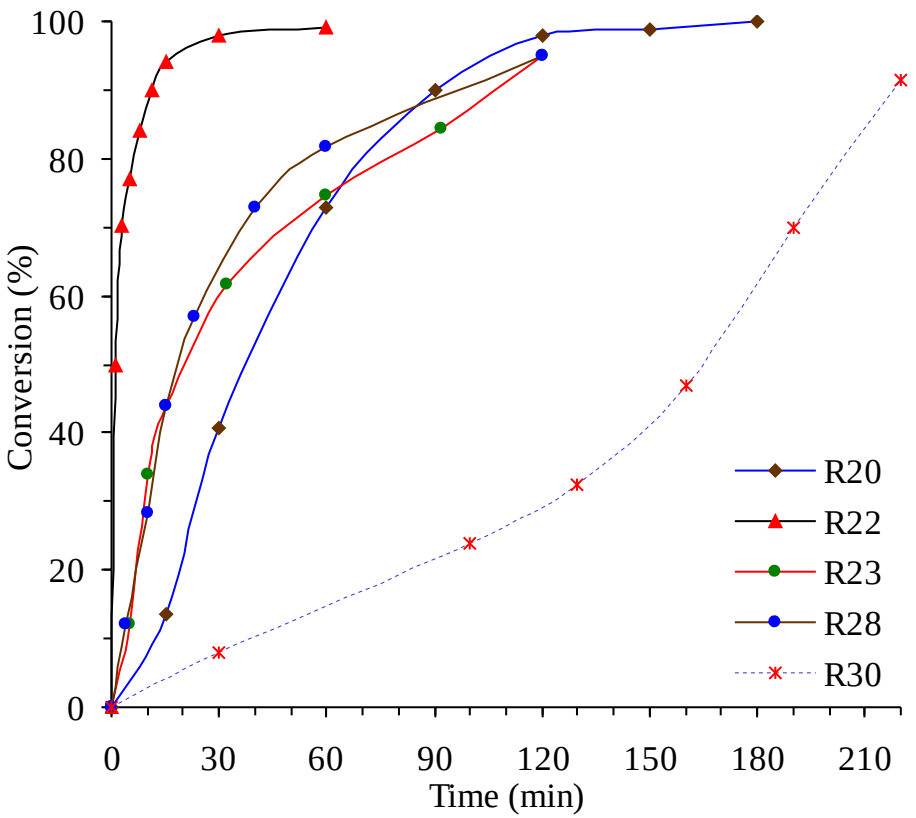
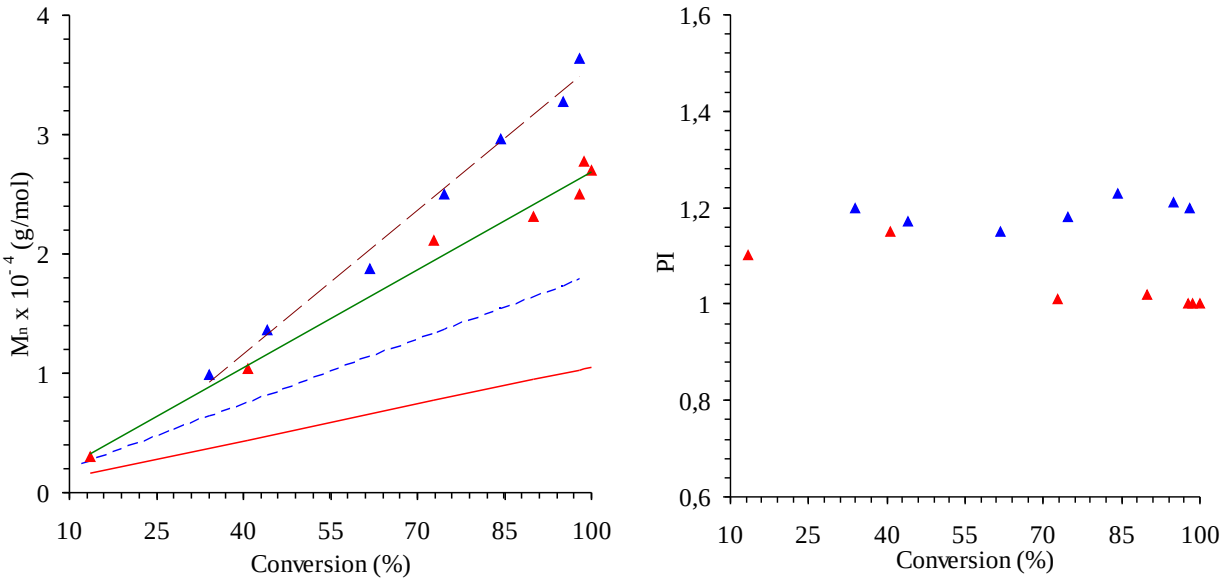


Figure 5.5. Influence of [PPD] on the evolution of monomer conversion as a function of reaction time. Detailed experimental conditions are given in Table 5.3.

The evolution of $\overline{M}_n$ as a function of conversion clearly shows the living character of this system (Figure 5.6a). The molecular weights are directly proportional to the conversion. The polydispersity values of polymers are very narrow and depend on the PPD level (Figure 5.6b). Increasing PPD concentration narrowed PI and decreased the molar mass of polymers (Table 5.3). The optimal condition for the preparation of poly(3-MDG) in RAFT-living miniemulsion with a PI of 1.05 and $\overline{M}_n$ in the range of 5 x 10^4 g/mol in a short reaction time of 100 min is successfully realized. The living radical polymerization of 3-MDG in solution

by using ATRP technique [8] yielded poly(3-MDG) with a PI of 1.2 and $\overline{M}_n$ of 1.3-2 x 10^4 g/mol in 5 h. The estimated $\overline{M}_n$ by GPC was two times higher than the calculated/theoretical value. This could be related to some factors, for example, GPC unit was calibrated with polystyrene standards. So the determined $\overline{M}_n$-values are poly(St) equivalents. Fukuda et al. made a comparison between two detection methods by means of refractive index and light-scattering on poly(3-MDG) [8]. They reported that the value of $\overline{M}_n$ detected by laser light-scattering (LLS) is about 2.4 times higher than that detected by refractive index (RI) detector. The detection system in this work is a combination of the two detection methods, RI online with MALLS. This could explain, why the measured $\overline{M}_n$ is higher than the calculated value by a factor 2.



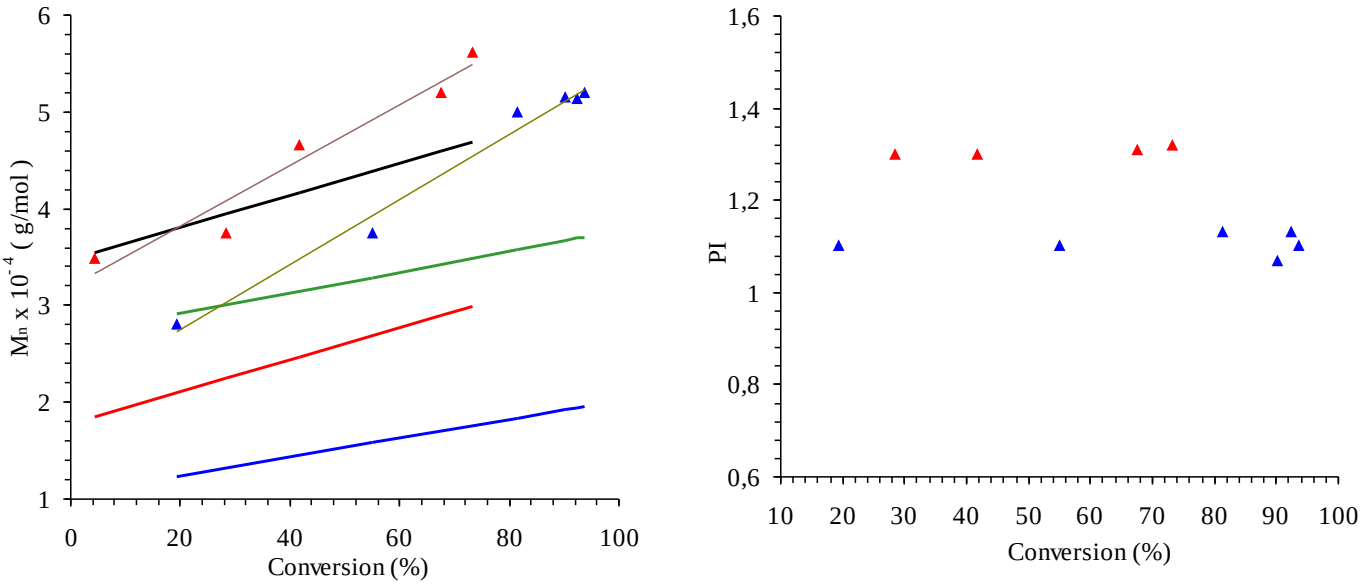
(a) (b)

Figure 5.6. Evolution of $\overline{M}_n$ and PI as a function of conversion for 3-MDG RAFT-miniemulsion polymerization at 70 °C with PPD;
a) $\overline{M}_n$ versus conversion, (▲) run R20, and (▲) run R23. The straight and doted lines represent the evolution of the theoretical $\overline{M}_n$-values versus conversion: (—) run R20, and (---) run R23.
b) PI versus conversion, (▲) run R20, (△) run R23.

Block copolymers-containing saccharide moieties could be of great importance in many applications. By using PPD as a RAFT agent, different block copolymers such as poly(3-MDG-*b*-BMA) were successfully synthesized in miniemulsion. BMA was selected as comonomer because it has relative low T_g-value of 20 °C, which can act as a soft component

in the copolymer compared to the rigid sugar moiety. Furthermore, BMA and 3-MDG exhibit relatively similar reactivity.

Figure 5.7a shows the increase of the polymer molecular weight after the addition of BMA. Furthermore, the gradual increase of $\overline{M}_n$ versus conversion is definitively an indication for the formation of block copolymer. For block copolymer, two theoretical molar mass were calculated, the first one based on the theoretical $\overline{M}_n$ of the first block and the other based on the experimental $\overline{M}_n$ found for the first block. The difference between $\overline{M}_{n,Th}$ and $\overline{M}_{n,Exp}$ is significantly small, if the calculation of $\overline{M}_{n,Th}$ is based on the experimental value of $\overline{M}_n$ for the first block. The difference is smaller at the beginning of polymerization in the second step than that at the end of polymerization. Also, PI of the block copolymer widens relatively than that of the poly(3-MDG) (Table 5.2 and Figure 5.7b). The formation of block copolymers was confirmed by ^{1}H and ^{13}C NMR and T_g measurements. The particle size of seed latexes increased by about 30-40 nm.



(a) (b)

Figure 5.7. Evolution of $\overline{M}_n$ and PI as a function of conversion for miniemulsion block copolymerization of 3-MDG and BMA at 70 °C with PPD (runs R21 and R24). See Table 5.3 for detailed experimental conditions.

a) $\overline{M}_n$ versus conversion, (▲) run R21, (▲) run R24, the straight lines represent the conversion evolution of the theoretical $\overline{M}_n$ (— run R21, and — run R24, the calculation based on the theoretical $\overline{M}_n$ of the first block), and (— run R21, — run R24, the calculation based on the experimental $\overline{M}_n$ of the first block);

b) PI evolution versus conversion, (▲) run R21, (▲) run R24.

An ABC-tri-block type polymer was successfully synthesized. In the first step, 3-MDF was polymerized in the presence of PPD, and then in a second step at about 90% conversion of 3-MDF, BMA was added to build the second block. An equal amount of KPS to that added in the first step was added. After 150 min reaction time, at 87% conversion of BMA, a new monomer (BA) was added to build the third block. Only 17 % of BA was polymerized to give a final tri-block copolymer with $\overline{M}_n$ of 9 x 10^4 g/mol and a PI of 1.3. The GPC chromatogram of the 3-MDF/BMA/BA tri-block copolymer is shown in Figure 5.8. This experiment shows the possibility to extend the polymer chain with different sequence type of monomers.

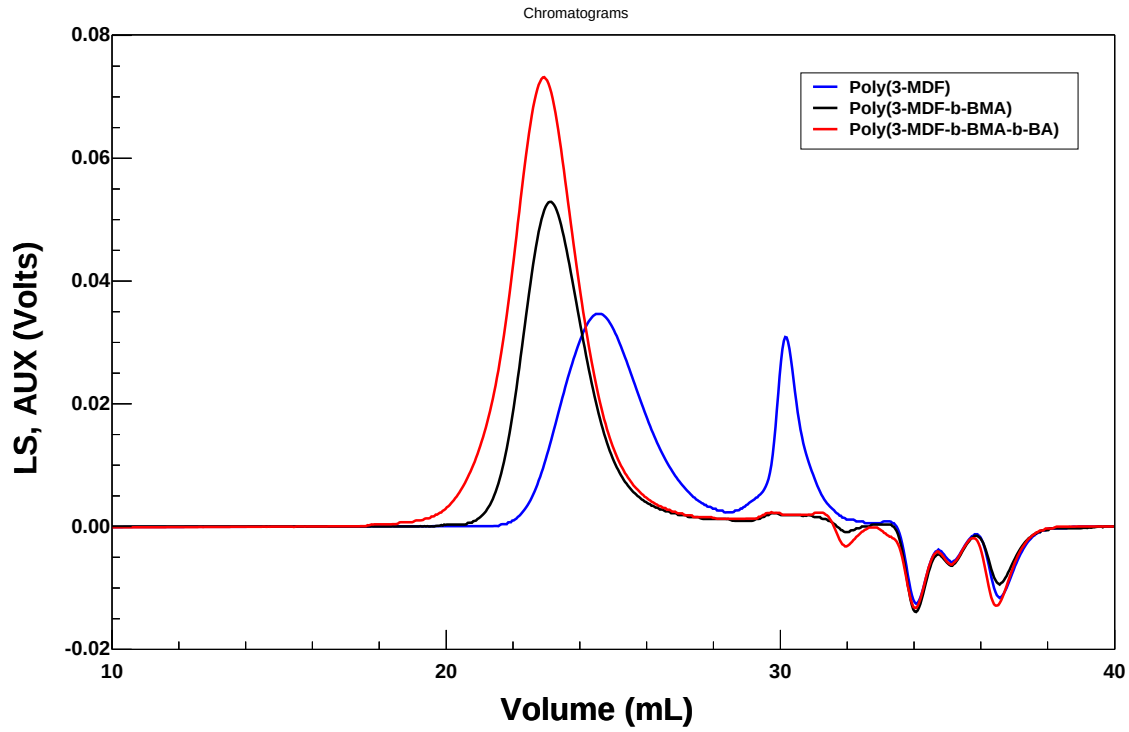


Figure 5.8. GPC chromatogram of run R30 (blue), R30´ (black) and R30´´(red) prepared by using of PPD.

The time evolution of the particles number during the polymerization is shown in Figure 5.9. At different PPD concentrations, the profile of N_p has the same tendency. The number of particles is approximately constant during the polymerization. The stabilization of N_p during the entire of polymerization is an important factor to obtain a good living character. Unstable N_p during polymerization could lead to an uncontrolled polymerization.

The block copolymerization was confirmed by NMR spectroscopy. In ^{13}C NMR spectrum of poly(3-MDG-*b*-BMA), the peak at 128 ppm represents the phenyl end group in poly(3-MDG), but this peak disappears at the high molecular weight as in the block copolymer

(Figure 5.10). Furthermore there are two peaks at about 180 ppm which represent the carbonyl groups of 3-MDG and BMA. The peak at 53 nm presents the methylene group, adjacent to the ester group, of BMA.

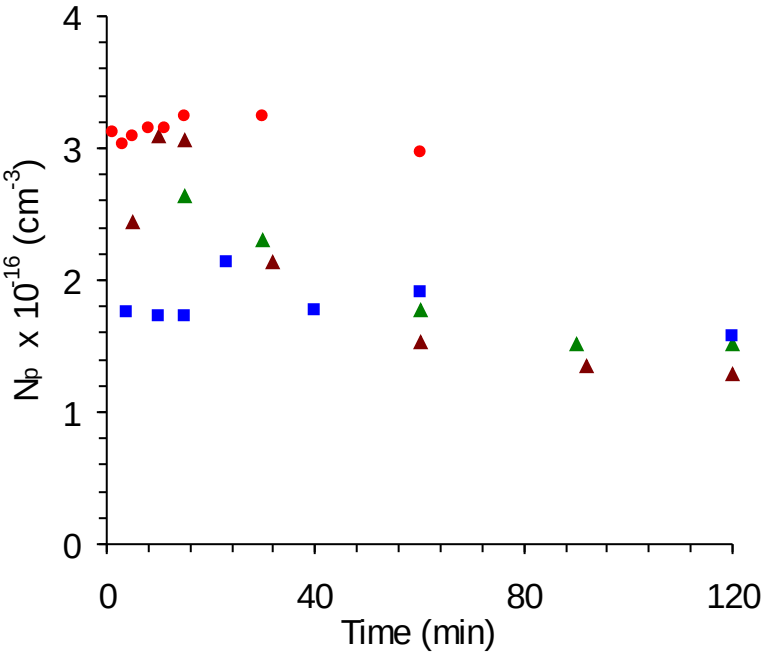


Figure 5.9. Total number of particles (N_p) against the polymerization time (min) for R20, ▲; R23, ▲; R22, ●; and R28, ■.

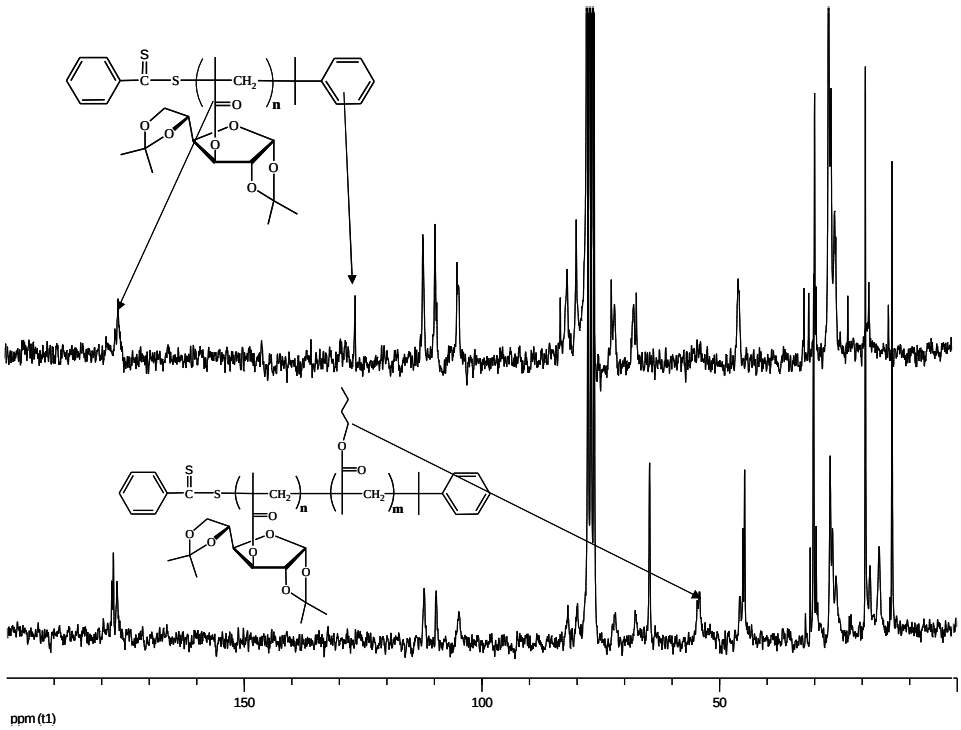


Figure 5.10. ^{13}C NMR spectrum of poly(3-MDG) and poly(3-MDG-*b*-BMA) block copolymer.

5.4.3 RAFT polymerization with 2-cyanoprop-2-yl dithiobenzoate (CPD)

2-cyanoprop-2-yl dithiobenzoate (CPD) was already used as RAFT agent in the polymerization of MMA in bulk and solution. It was found that this agent exhibits a good living character [13]. Poly(MMA) was obtained with a PI in the range of 1.1 - 1.4 and $\overline{M}_n$ of about $5x10^4$ g/mol. Contrarily, the use of CPD in miniemulsion polymerization of 2-ethyl hexyl methacrylate (2-EHMA) and BMA yielded polymers with a low PI in the range of 1.3 - 1.5 [14]. In these cases, the effect of the polymerization system (homogeneous or heterogeneous) on the efficiency of RAFT agents is clearly observed. The suitability of CPD as RAFT agent in miniemulsion polymerization of 3-MDG was also investigated.

Table 5.4. CPD-RAFT miniemulsion polymerization of 3-MDG at 70 °C.

	EXP.	Monomer	RAFT (g)	Conv. (%)	Time (min)	D (nm)	$\overline{M}_{n,Th}$ x10^{-4} g/mol	$\overline{M}_{n,Exp}$ x10^{-4} g/mol	PI
First step	R25	3-MDG	0.1	99,3	180	312	3.83	5.45	1.78
	R29	3-MDG	0.2	30	360	225	0.52	2.09	1.32
Second step	R25´	BMA	--	60	180	320	5.44	7.51	1.84
	R29´	BMA	--	54	120	257	2.25	15.10	1.59

The amounts of monomer (15 g), water (135 g), SDS (0.24 g), HD (0.50 g), 0.08 g KPS and $NaHCO_3$ (0.1 g) were hold constant for all the runs. In the second polymerization step, further 0.08 g KPS was added as initiator.

As shown in Table 5.4, two experiments were carried out with two different concentrations of CPD. At high CPD concentration as in R29, the rate of polymerization retarded significantly and only 30% of 3-MDG was polymerized in a reaction time of 360 min. The formed polymer has a $\overline{M}_n$ 4 times higher than the theoretical value, $\overline{M}_{n,Th}$, and a PI of 1.32. The decrease of [CPD] leads to increase the conversion (99.3%) in a short polymerization time of 180 min, but the PI of the formed polymer is more broadly (1.78). This result is similar to the results founded by Moad et al. [13] and coincided more or less with the results of Schork et al. [14-15].

I suppose that 2-cyanoprop-2-yl free radical, as a good leaving group due to its low size and its high hydrophilicity, could be easily diffuse out the polymer particle. This leads to a decrease the number of free radicals in the particles and consequently retarded the rate of polymerization and also increases the polydispersity of the formed polymer.

Two attempts were conducted to synthesize block copolymer by RAFT miniemulsion polymerization. The latexes R25 and R29 were used as seed for the second polymerization

step (R25´ and R29´). The increase of $\overline{M}_n$ by the second polymerization step is a proof for the block formation (Figure 5.11). Nevertheless, PI of the produced block copolymers was in the range of 1.6-1.9. These values could be related to the high PI in the first step.

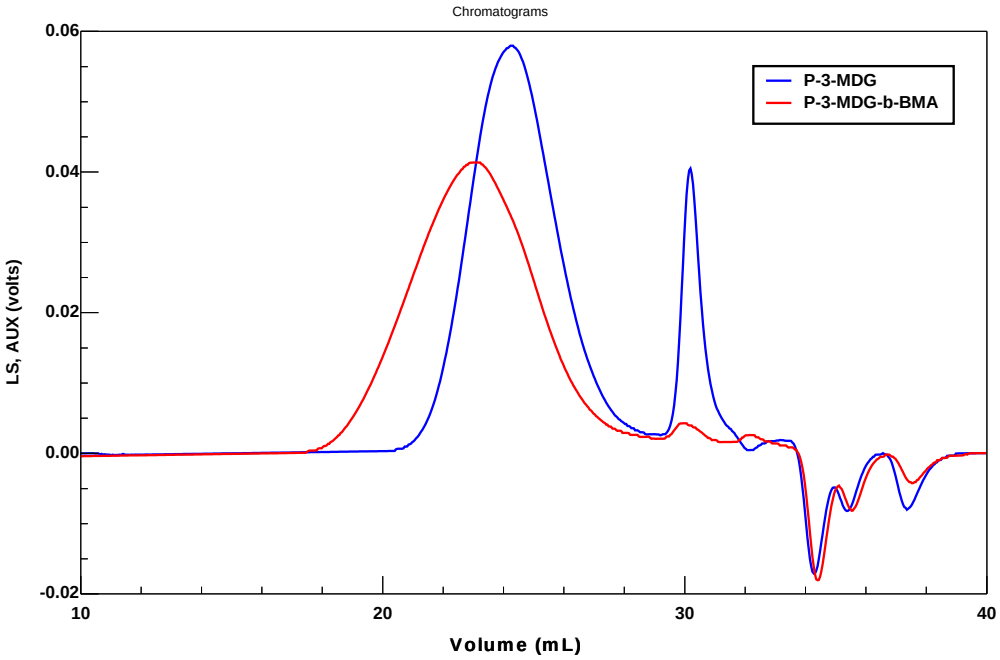
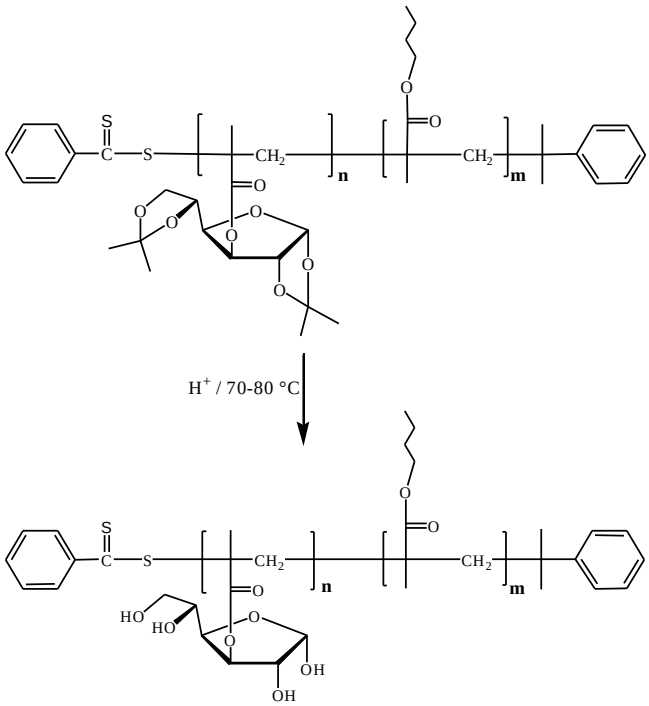


Figure 5.11. GPC-chromatogram of poly(3-MDG) run R25 (blue) prepared by using of CPD, and poly(3-MDG-*b*-BMA) R25´ (red). The blue peak at 30 ml volume is from the THF.

5.4.4 Acid hydrolysis of the (3-MDG-*b*-BMA) block copolymer colloid

The aim was the preparation of polymer particles exhibiting a core/shell morphology, in which the shell is composed from hydrophilic sugar moieties. This was conducted through the acid hydrolysis of the isopropylidene groups of the sugar derivatives of the latex. The deprotection of these isopropylidene groups of poly(3-MDG) was reported in many works in order to prepare water soluble glycopolymer [8]. The synthesized block copolymer particles, poly(3-MDG-*b*-BMA) were deprotected in order to obtain beside the hydrophobic sequence (BMA) a sugar based hydrophilic sequence (Scheme 5.2). The yielded block copolymer exhibits an amphiphilic character, in which the hydrophobic parts form the core of the particle and the hydrophilic one migrate to its natural aqueous medium. Consequently, a displacement to the water phase occurs, building the shell of the latexes.



Scheme 5.2. Schematic presentation of acid deprotection of 3-MDG forming an amphiphilic block copolymer.

The first attempt was conducted by the addition of concentrated HCl dropwise till pH 1.5 after the end of the second step of polymerization. The mixture was kept under stirring for 24 h at 70 °C. Due to the complete hydrolysis, the latex has been gelatinized. The particle size of the hydrolyzed latex was increased from 200 to 498 nm with PDI (D_w/D_n) of 0.234. The gelatinous latex forms film at room temperature. This film is transparent, vitreous and brittle.

The block copolymer composition of 3-MDG/BMA was (77/23 wt.%). The high content of 3-MDG in the block copolymer gives it a high rigidity.

Another attempt was carried out by diluting 15 g latex with 15 g water and 8 ml conc. HCOOH. The pH of latex was 1.5. The latex was kept under stirring for 24 h at room temperature. After one day, the latex was neutralized with conc. NH_3. The emulsifier and the rest of monomer(s), and initiator were removed through dialysis. The particle size of the hydrolyzed latex increased form 166.3 to 700 nm and the PDI from 0.128 to 0.311. Gelation was not observed. With neutralization the latex became more viscous. Figure 5.12 shows a TEM-micrograph of hydrolyzed latex with a particle size of 700 nm.

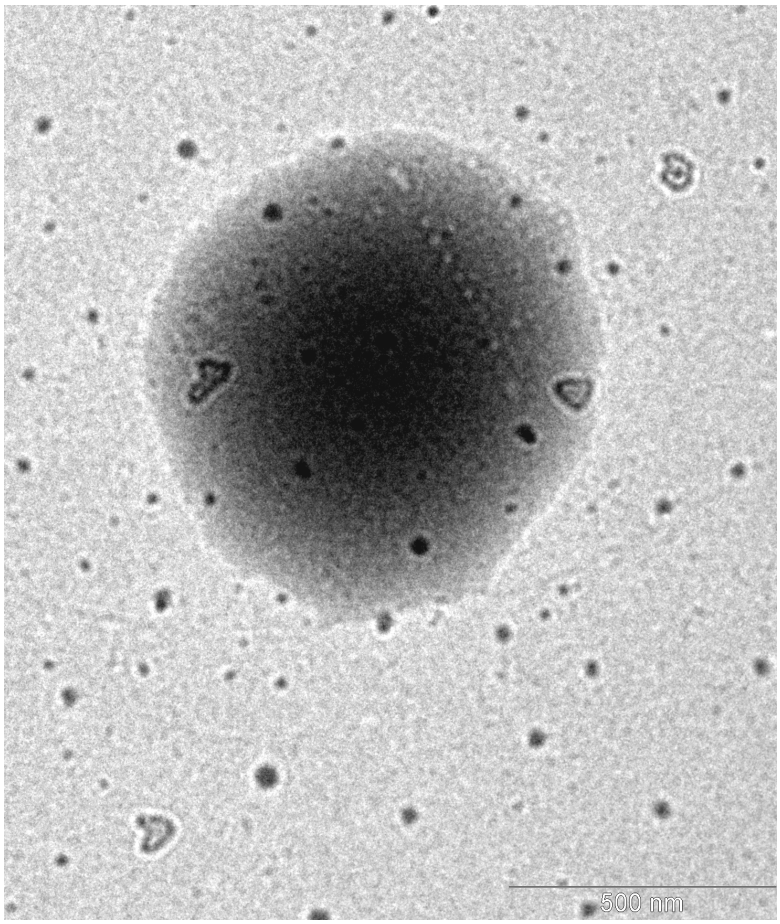


Figure 5.12. TEM-micrograph of hydrolyzed sugar latex with end particle size of 700 nm.

In this case the end latexes exhibit a core/shell morphology, in which the outer part of the particle (shell) is composed from the hydrophilic glucose moieties. Furthermore, no gelation was observed. After neutralization, the latex became more viscous, due probably to the intermolecular hydrogen bonds interactions between the hydrophilic polymer “hair”.

5.5 Conclusion

Well designed saccharide containing polymers were prepared via reversible addition-fragmentation transfer (RAFT) polymerization in miniemulsion. Polymerization of 3-MDG in the presence of PED showed no living character and the obtained polymers had $\overline{M}_n$ of about 2.5 x 10^5 g/mol and PI in the range of 1.6 to 1.8. Polymerization in the presence of CPD displayed a living character, but a high CPD concentration was required to form polymers with low polydispersity. Poly(3-MDG) and poly(3-MDF) polymers were extended in a second polymerization step with other block monomers such as BMA and BA. The best results were obtained in the presence of PPD-RAFT agent. The preparation of poly(3-MDG) and poly(3-MDF) in miniemulsion with a PI of 1.05 and $\overline{M}_n$ in the range of 5 x 10^4 g/mol in a short reaction time of 100 min were successfully achieved. Finally, amphiphilic block copolymers were successfully obtained by the deprotection of saccharide moieties by means of acid hydrolysis of the isopropylidene groups.

5.6 References

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SUMMARY

The challenge claimed at the beginning of this thesis by the synthesis of new polymers colloids partially based on renewable resources, such as **low molecular carbohydrates**, and using ecological processes such as the **emulsion polymerization** has been successfully reached. The tailor made new water polymer dispersions showed interesting thermal, mechanical and rheological properties.

To achieve our aim, this work has dealt with the free radical emulsion copolymerization of monosaccharide-based monomers, and alkyl (meth)acrylates. The choice of cheaply and industrially available monosaccharide resources such as D-Glucose and D-Fructose and their chemical modifications by adequate synthesis to saccharide derivatives led to 3-MDG (3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose), and 3-MDF (3-*O*-methacryloyl-1,2:4,5-di-*O*-isopropylidene-α-D- fructopyranose), which were very suitable for the emulsion polymerization, due to their chemical stabilities and their oily natures. These sugar acrylates were successfully obtained in a two-steps synthesis and in a high yield. These encouraging results could be very favorable for possible industrial applications of such monomers. On the other hand, commercially available and soft comonomers such as butyl acrylate (BA) and butyl methacrylate (BMA) as copolymerization partner to the rigid sugar components were selected.

The choice of the emulsion process showed a great effect on the final latex properties as well as on the properties of the precipitated corresponding polymer. We have investigated the copolymerization behavior of 3-MDG and BA by the most industrially applicable process such as the **semicontinuous processes**. From this point of view we have used the semicontinuous emulsion polymerization, with its two main techniques, the so-called monomer feed and pre-emulsion addition. The properties of the final latexes have been strongly affected by the variation of some reaction parameters such as the rate of addition, surfactant concentration and type, initiator concentration and type.

The second chapter dialed with the semicontinuous emulsion copolymerization of 3-MDG/BA by **monomer addition** technique and its influence on the reaction kinetic and final latex properties. Different latexes with interesting colloidal properties were synthesized by varying the polymerization conditions.

The third chapter concerned with semicontinuous emulsion copolymerization of 3-MDG/BA by **pre-emulsion** addition technique. The effects of the polymerization variables on the colloidal (particle size and particle size distribution), thermal (glass transition temperature),

mechanical (film formation and tensile strength), and rheological (flow behavior) properties were established.

Another interesting route for producing polymer colloids is the **miniemulsion** polymerization. The glucose methacrylate, 3-MDG, with its low water solubility was obeyed well the mechanism of the miniemulsion polymerization, in which the nucleation, occurs mainly in the monomer droplets. Under defined conditions, the so-called one-to-one droplets: particles copy process was obtained. Some important reaction parameters such as the emulsifier type and concentration, the initiator type and concentration as well as the costabilizer (hydrophobic agent) concentration showed a strong influence on the latex properties.

Because the initiation (nucleation), propagation, termination and transfer reactions occur mainly in the monomer droplets by miniemulsion polymerization, this motivated us to use the **living/controlled radical polymerization** in miniemulsion as a new technique to obtain polymer colloids containing saccharide moieties with a desired microstructure and exhibiting narrow molecular-weight distribution. The **RAFT technique in miniemulsion** was chosen to achieve this goal. Three RAFT agents were used to control the molecular weight and its distribution. Tailored made polymers with a defined molecular weight and very narrow polydispersity were synthesized. The main advantages of the used RAFT technique in miniemulsion can be concluded as follows:

- Ø the use of only one agent to control the polymerization
- Ø choice possibility of an adequate RAFT agent for an effective control over the growth of living chains
- Ø applicability to a wide range of monomers, such as acrylate, methacrylate, styrene, etc.
- Ø shorter polymerization time in comparison with ATRP or SFRP
- Ø high molecular weight polymer with narrow polydispersity
- Ø high monomer conversion, over 99%
- Ø polymerization at a moderate temperature, 50-80 °C
- Ø easily removable end group after polymerization through photo-oxidation
- Ø synthesis of block copolymers by extending the polymer chains with other comonomers

RAFT miniemulsion of 3-MDG and 3-MDF with cumyl dithiobenzoate (2-phenylprop-2-yl dithiobenzoate**,** PPD) yielded polymer colloids, in which the formed homopolymers exhibit low polydispersity indexes, PI < 1.2. Moreover, we have achieved for the first time by this technique the preparation of sugar based **block copolymers** within the polymer colloids such

as poly(3-MDG-*b*-BMA), poly(3-MDG-*b*-BA), poly(3-MDF-*b*-BMA), and tri-block copolymers poly(3-MDF-*b*-BMA-*b*-BA).

We finally succeeded the deprotection of the glucose repeat units within the polymer colloids, by means of removing the isopropylidene groups, modifying the properties of the block copolymers and yielding final latexes with a **core/shell morphology**. The deprotection of poly(3-MDG-*b*-BMA) yielded poly(3-*O*-glucose-*b*-BMA), where the formed block copolymer has an amphiphilic character. The amphiphilic properties can be varied by varying the polymer composition by means of the variation of the sequence length of each block, and consequently the draft of hydrophilic/hydrophobic balance. The corresponding hydrolyzed latex is composed from the hydrophobic BMA block as core and the hydrophilic glucose block as shell. In comparison to other surface functionalization techniques of the latexes, in which the hydrophilic groups covered only the surface of the particles, the RAFT-miniemulsion process allows to obtain polymer particles with narrowed hydrophilic polymeric chains on their surfaces, which are extended in the aqueous phase and anchored chemically to the core.

The combination of using monomers based on renewable resources and environmentally friendly emulsion polymerization process offers many advantages over the classical polymerization techniques, enhances the possibility for an industrial scale up and presents new applications of the final polymeric materials.

Optimization of the synthesis of these new polymer colloids through RAFT-miniemulsion and further analytical investigations are needed for more comprehension of this system. These were not the scope of this study and can be interesting tools for the future works. The development of new industrial applications could be helpful to commercialize such new and very much promising polymeric materials.

Symbols and Abbreviations

Symbols

d	diffusion coefficient	[m^2/s]
D	particle diameter	[nm]
[I]	initiator concentration	[mol/L]
k_d	initiator decomposition rate constant	[1/s]
k_p	propagation rate constant	[L/mol·s]
k_t	termination rate constant	[L/mol·s]
k_{tr}	transfer rate constant	[L/mol·s]
C_{tr}	chain transfer constant or coefficient	[L/mol·s]
M	molar mass	[g/mol]
$\overline{M}_n$	number-average molecular weight	[g/mol]
$\overline{M}_w$	weight-average molecular weight	[g/mol]
PI	polydispersity index ($\overline{M}_w/\overline{M}_n$)	[-]
[M]	monomer concentration	[mol/L]
$[M]_p$	monomer concentration in the polymer particle	[mol/L]
$\bar{n}$	average number of radicals per particle	[–]
N_p	number of particle per unit volume	[$1/m^3$]
NA	Avogadro's number	[1/mol]
PDI	polydispersity index (D_w/D_n)	[–]
PSD	particle size distribution	
[$R^\bullet$]	radical concentration	[mol/L]
T	absolute temperature	[K]
T_g	glass transition temperature	[K]
V	volume	[m^3]
x	fractional conversion	[–]
X	mole fraction	[–]
TS	solid content	[wt-%]

Greek Symbols

λ	wavelength	[nm]
ρ	density	[g/ml]

σ	standard deviation	[–]
η_0	viscosity with low shear rate	[Pa s]
η_∞	viscosity with high shear rate	[Pa s]
γ	surface tension	[N/m]

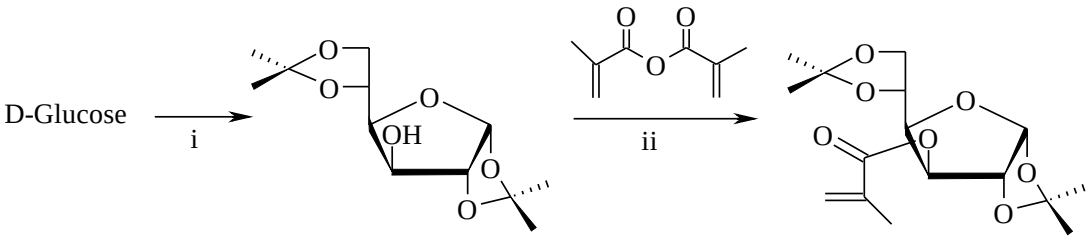
Abbreviations

AIBN	α,α'-azobis(isobutyronitrile)
BA	butyl acrylate
poly(BA)	poly- butyl acrylate
BMA	butyl methacrylate
DAG	1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose
DLS	dynamic light scattering
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
KPS	potassium peroxodisulfat
3-MDG	3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose
3-MDF	3-*O*-methacryloyl-1,2:4,5-di-*O*-isopropylidene-α-D- fructopyranose
poly(3-MDG)	poly(3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose)
poly(3-MDF)	poly(3-*O*-methacryloyl-1,2:4,5-di-*O*-isopropylidene-α-D- fructopyranose)
MEK	methyl ethyl ketone
MMA	methyl methacrylate
poly(MMA)	poly-methyl methacrylate
NaCl	sodium chloride
NMR	nuclear magnetic resonance spectroscopy
poly(St)	polystyrene
RAFT	reversible addition-fragmentation transfer
RI	refractive index
SDS	sodium dodecyl sulfate
SEC	size exclusion chromatography
TEM	transmission electron microscopy
THF	tetrahydrofuran
HCl	hydrochloric acid
rpm	rounds per minute
US	ultra sound

Appendix 1. Synthesis of 3-MDG monomer

The synthesis of 3-MDG monomer, i.e. 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, is well known and was reported in many articles [27-37, chapter 1]. As shown in Scheme 1, starting from D-glucose, 3-MDG can be obtained in two-steps reaction. Firstly, D-glucose reacted with acetone in acidic medium to protect the hydroxyl groups at C-1,2 and C-5,6 positions of the glucose moiety giving 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (DAG). The yield of DAG is over 70% based on the used D-glucose. DAG is commercially available [Fluka]. Esterification of DAG with methacrylic acid anhydride in pyridine leads to 3-MDG. To a solution of 300g DAG (1.15 mol) in 150 ml absolute pyridine and 300 ml petroleum ether, 275 ml (0.53 mol) methacrylic acid anhydride was added dropwise at room temperature. The mixture was heated at 65 °C for 3.5 h and for another 1 h after addition of 1000 ml of water. Then the mixture was allowed to get cool to room temperature overnight. The organic phase was separated by separating funnel and the aqueous phase was washed thee times with petroleum ether (boiling range 30-70°C). The combined extract (organic phase) was washed three times with 500 ml of 5% sodium hydroxide solution and three time with 300 ml of distilled water. The organic phase was finally dried over anhydrous sodium sulfate. Ca. 100 mg methylene blue was added to the organic phase as inhibitor before removing the solvent. The crude product was purified by distillation at 135°C and under reduced pressure (10^{-2} mbar). For long storing and easy handling, the oily 3-MDG was recrystallized with petroleum ether (one part 3-MDG+half part petroleum ether) at -10°C overnight. The yield of reaction is ca. 80%. Another procedure was used to prepare 3-MDG, 300 g DAG dissolved in 190 ml pyridine and continued as before. The same yield is obtained. For the purification of the crude product, flash silica gel chromatography with a 7:2:1 ethyl acetate : toluene : methanol mixture eluent can be used.

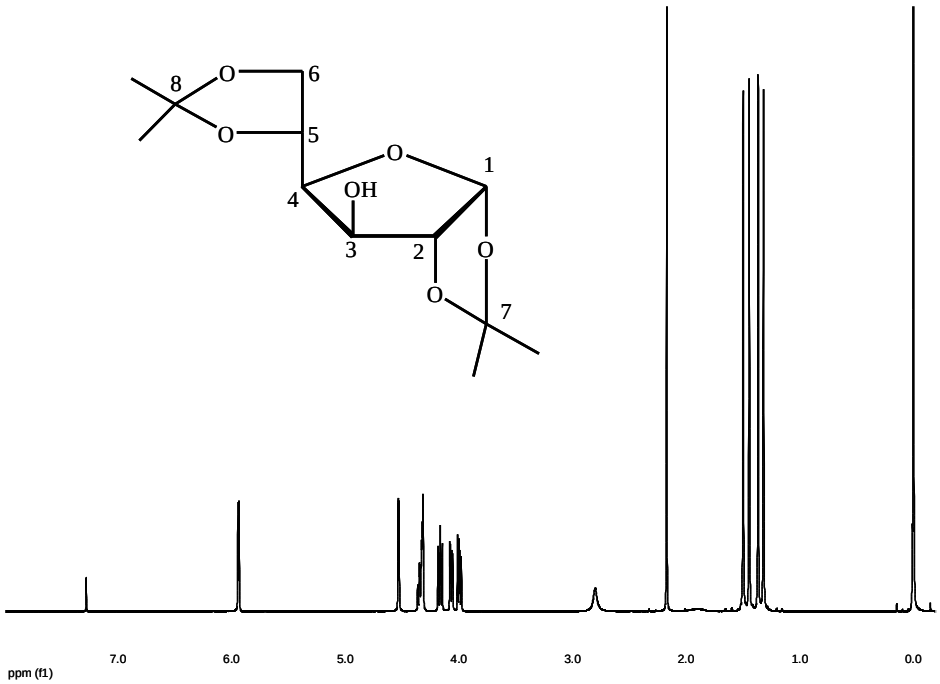
It was possible to prepare 1000g 3-MDG in a laboratory scale.



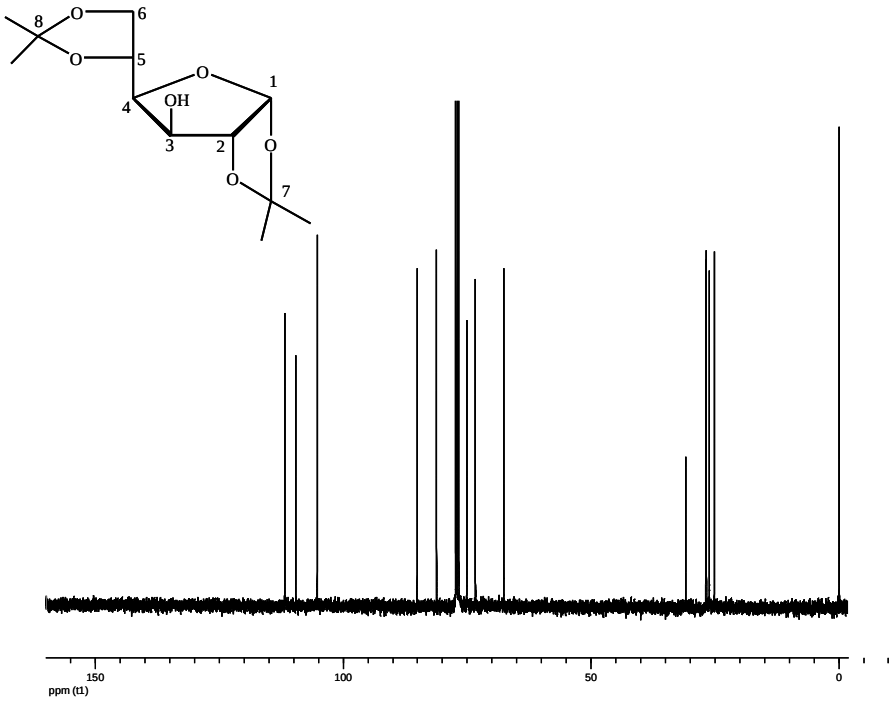
i) CH_3COCH_3 / $ZnCL_2$/ H_3PO4, ii) pyridine/ petroleum ether, 65 °C, 4h

Scheme 1. Synthesis of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3-MDG).

Appendix 2. ^{1}H and ^{13}C NMR spectra of DAG

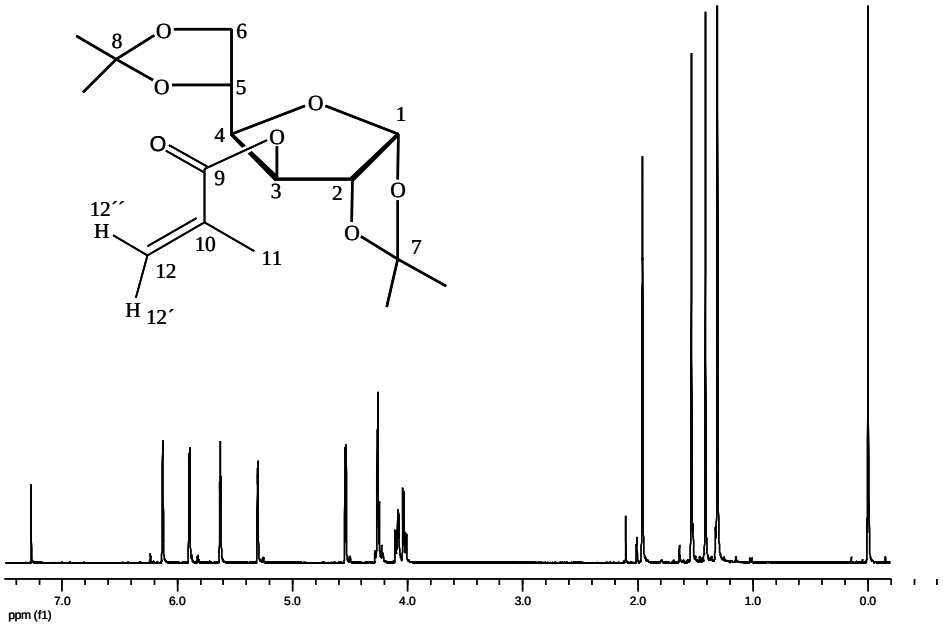


^{1}H NMR (400,1 MHz, $CDCl_3$): δ (ppm) = 1.31, 1.37, 1.44, 1.50 (s, 12 H, isopropylidene-H), 2.8 (s, 1 H, -OH), 3.99 (m, 1 H, H-3), 4.04 (m, 1 H, H-4), 4.10 (m, 1 H, H-5), 4.32 (m, 2 H, H-6), 4.53 (d, 1 H, H-2), and 5.94 (d, 1H, H-1). [2.17, s, 2H, H_2O]

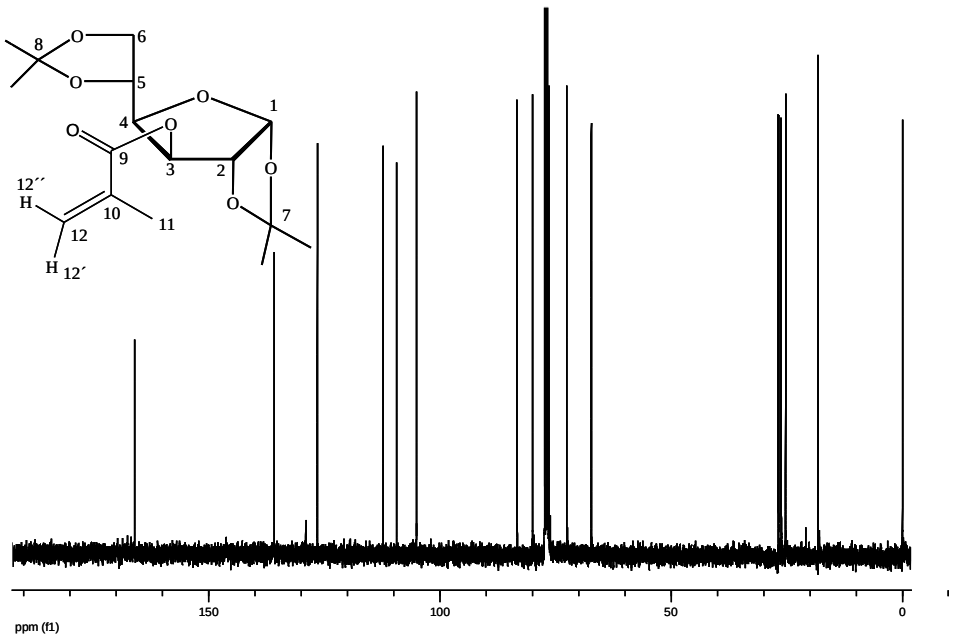


^{13}C NMR (100, 6MHz, $CDCl_3$): δ (ppm) = 25.1-26.8 (4 isopropylidene-C), 67.6 (C-6), 73.3 (C-3), 75 (C-4), 81.1 (C-5), 85.1 (C-2), 105.2 (C-1), 109.6 (C-7), 111.8 (C-8).

Appendix 3. ^{1}H and ^{13}C NMR spectra of 3-MDG

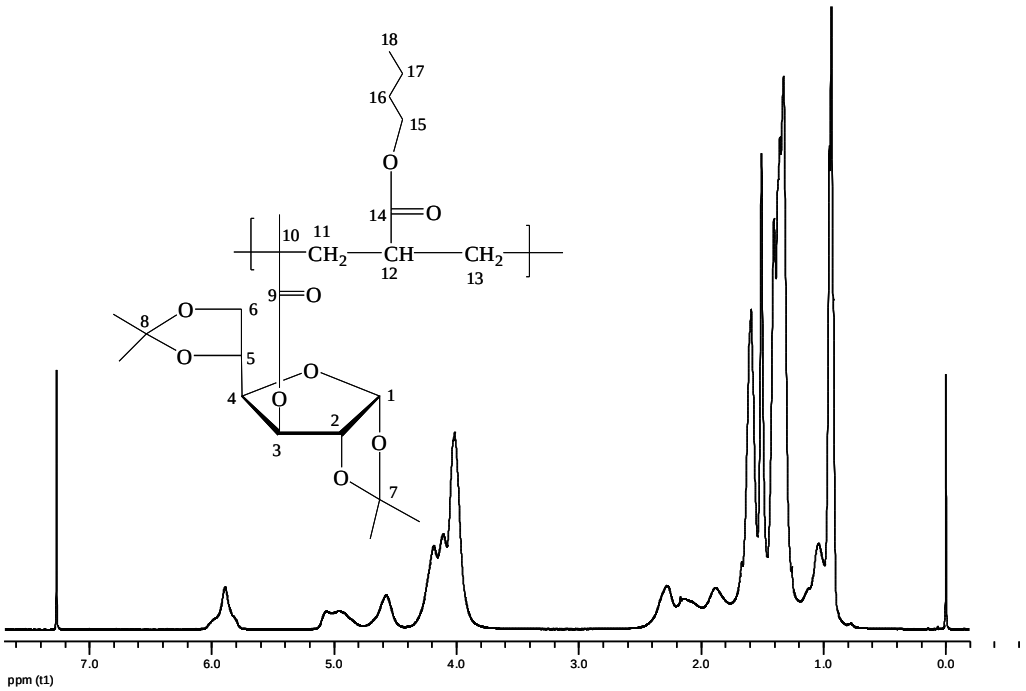


^{1}H-NMR (400,1 MHz, $CDCl_3$): δ = 1.31, 1.41, 1.53 (s, 12 H, isopropylidene-H), 1.96 (s, 3 H, H-11), 4.04 (m, 1 H, H-2), 4.26 (m, 1 H, H-3), 4.39 (m, 2 H, H-6), 4.54 (d, 1 H, H-5), 5.30 (d, 1 H, H-4), 5.62 (t, 1 H, H-12''), 5.90 (d, 1 H, H-1), 6.13 (s, 1 H, H-12').

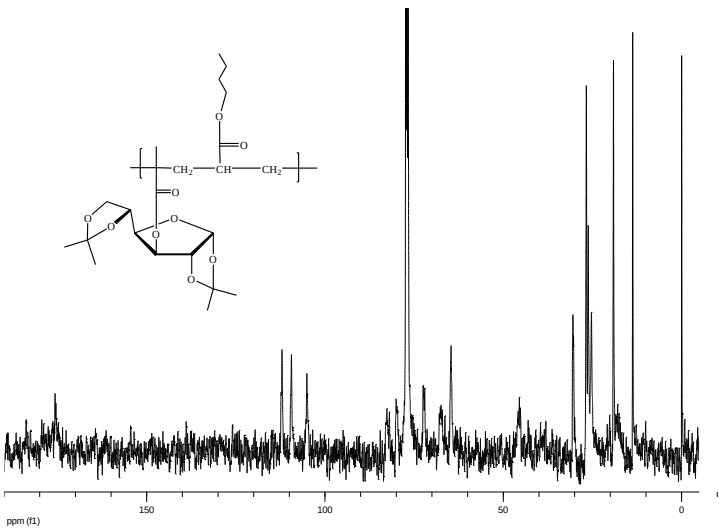


^{13}C NMR (100, 6MHz, $CDCl_3$): δ = 25.1-26.8 (4 isopropylidene-C), 67.6 (C-6), 73.3 (C-4), 75 (C-3), 81.1 (C-5), 85.1 (C-2), 105.2 (C-1), 109.6 (C-7), 112.9 (C-8), 126.5 (C-12), 135.8 (C-10), 165. 9 (C-9).

Appendix 4. ^{1}H and ^{13}C NMR spectra of 3-MDG/BA Copolymer



^{1}H NMR (400,1 MHz, $CDCl_3$): δ = 3.8-5.2 (8 H, H-2, H-3, H-4, H-5, 2 x H-6+2 x H-15), 5.90 (1 H, H-1).



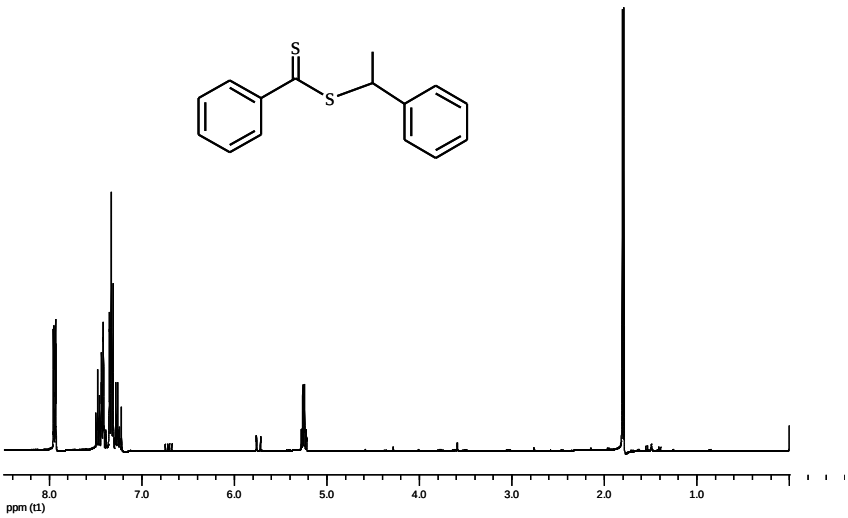
^{13}C NMR (100, 6MHz, $CDCl_3$): δ = 25.1-26.8 (4 isopropylidene-C), 67.6 (C-6), 73.3 (C-4), 75 (C-3), 81.1 (C-5), 85.1 (C-2), 105.2 (C-1), 109.6 (C-7), 112.9 (C-8), 126.5 (C-12), 135.8 (C-10), 165. 9 (C-9).

Appendix 5. Preparation and characterization of RAFT-agents

1. 1-phenylethyl Dithiobenzoate (PED)

RAFT agent was prepared in two steps as described in the literature (chapter 5) [13]. In the first step dithiobenzoic acid was synthesized from benzyl chloride. Benzyl chloride (128 g, 1 mol) was added dropwise to a stirred suspension of elemental sulfur (64 g, 1 mol) and sodium methoxide (108 g, 1 mol) in dry methanol 300 ml at 70 °C. The mixture was stirred overnight. After cooling the reaction mixture was filtered and methanol was removed under reduced pressure. The organic oily brownish residue was taken up in water. The dispersion was re-filtered. The water solution of sodium dithiobenzoate was treated with hydrochloric acid. Dithiobenzoic acid was extracted with diethyl ether, then dried with sodium sulfate and finally diethyl ether was evaporated under reduce pressure.

In the second step, dithiobenzoic acid (6 g, 0.039 mol), styrene (6 ml, 0.053 mol) and carbon tetrachloride (30 ml) were combined and the mixture heated at 70 °C for 4 h. The resultant mixture was concentrated on a rotary evaporator and the residue subjected to column chromatography on alumina (activity III, 6% water content) with petroleum spirits (b.p. 40-60 °C) as eluent to give 1-phenylethyl dithiobenzoate (4.4 g, 43.4%). The product was analyzed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



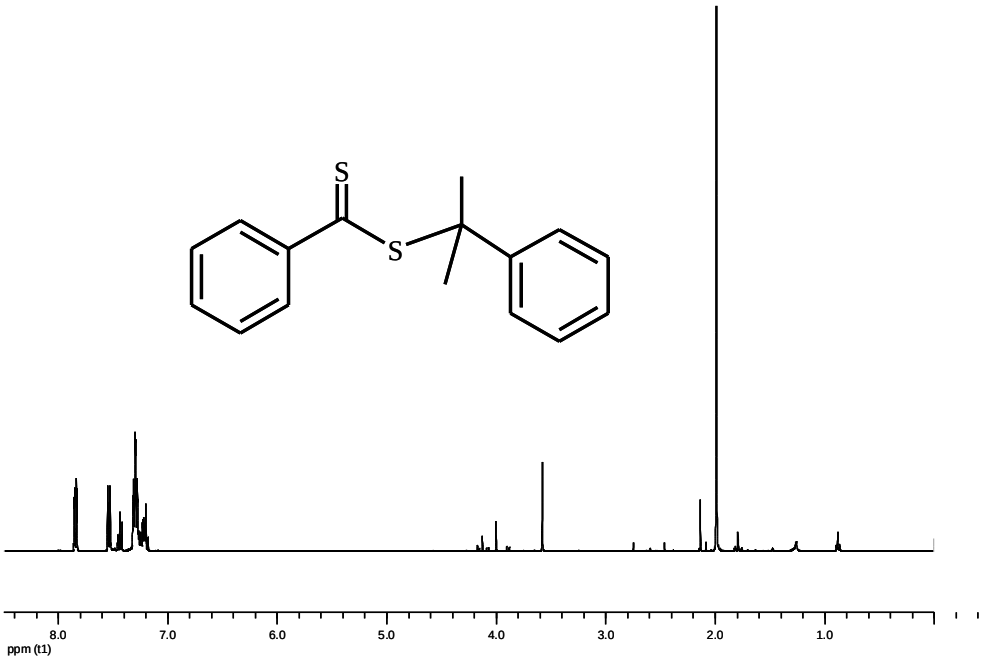
^{1}H NMR (100,6 MHz, $CDCl_3$): δ = 1.8 (d, 3H, CH-CH_3); 5. 28 (q, 1H, CH-CH_3); 7.2-7.5 (m, 8H, ArH);7.95 (d, 2H, o-ArH of dithiobenzoate).

^{13}C NMR ($CDCl_3$): δ = 20.7 (1C, CH_3); 50.32 (1C, CH-); 126-144 (12C, 2 phenyl groups).

EI mass spectrum: found, 258.05 (M^+); $C_{15}H_{14}S_2$ requires 258.05.

2. 2-Phenylprop-2-yl Dithiobenzoate (PPD)

A mixture of dithiobenzoic acid, which was prepared as described before, (6 g, 0.039 mol), α-methyl styrene (6 ml, 0.053 mol) and carbon tetrachloride (30 ml) was heated at 70 °C for 4 h. The resultant mixture was concentrated on a rotary evaporator and the residue subjected to column chromatography on alumina (activity III, 6% water content) with n-hexane as eluent to give 2-phenylprop-2-yl dithiobenzoate (4.4 g, 32.6%). The product was analyzed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



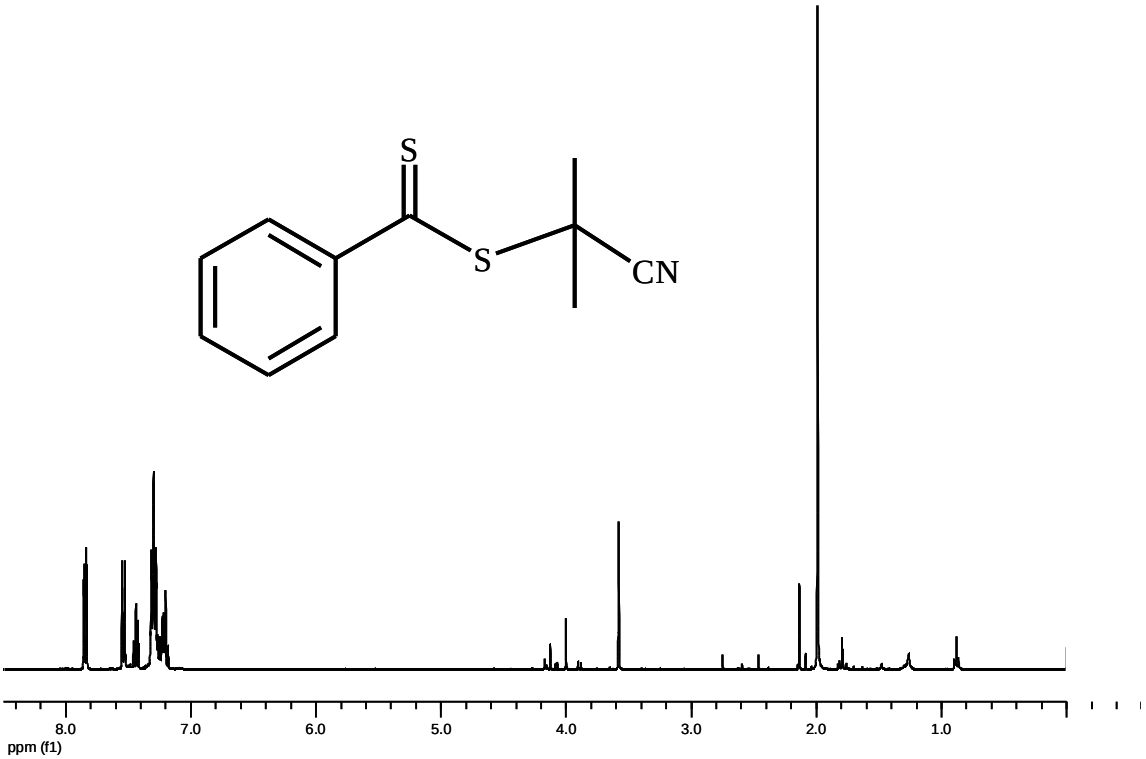
^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 6H, C-$(CH_3)_2$); 7.2-7.6 (m, 8H, ArH); and 7.8 (d, 2H, o-ArH of dithiobenzoate).

^{13}C NMR ($CDCl_3$): δ = 28.5 (2C, $(CH_3)_2$); 56.8 (1C, C-S-); 126-146 (12C, 2 phenyl groups).

EI mass spectrum: found, 272.08 (M^+); $C_{16}H_{16}S_2$ requires 272.03.

3. 2-Cyanoprop-2-yl dithiobenzoate (CPD)

A mixture of 2-phenylprop-2-yl dithiobenzoate (PPD), which was prepared as described before, (4 g, 0.0146 mol) and 2,2´-azobisisobutyronitrile (AIBN, Fluka) (4.8 g, 0.029 mol) in benzene (40 ml) was heated under reflux at 80 °C for 24 h. The resultant mixture was concentrated on a rotary evaporator and the residue subjected to column chromatography on silica gel with n-hexane : diethyl ether (9:1) as eluent. The yield of 2-cyanoprop-2-yl dithiobenzoate was (3 g, 90%). The product was analyzed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.

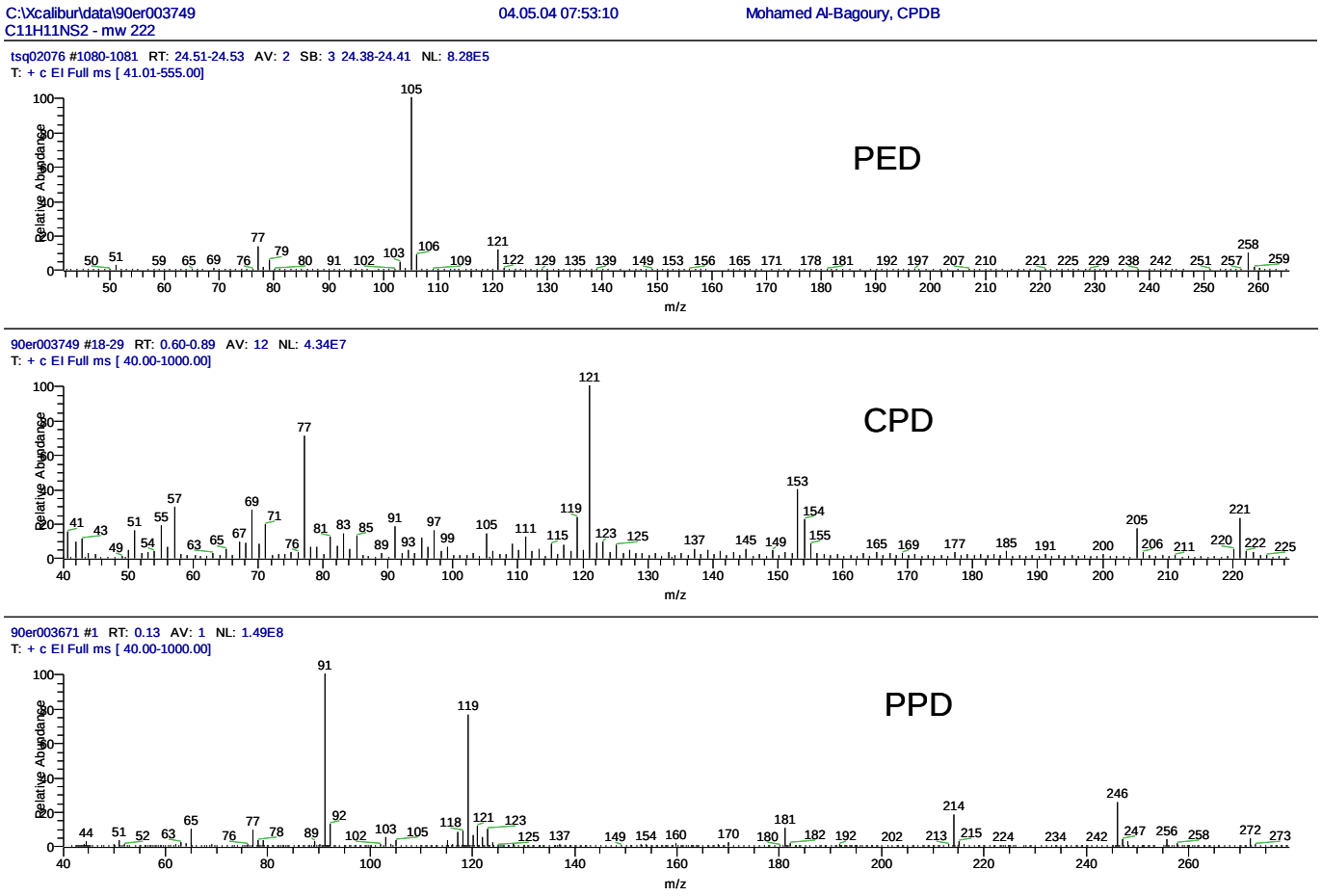


^{1}H NMR ($CDCl_3$): δ = 2.03 (s, 6H, C-$(CH_3)_2$); 7.2-7.6 (m, 8H, ArH); and 7.8 (d, 2H, o-ArH of dithiobenzoate).

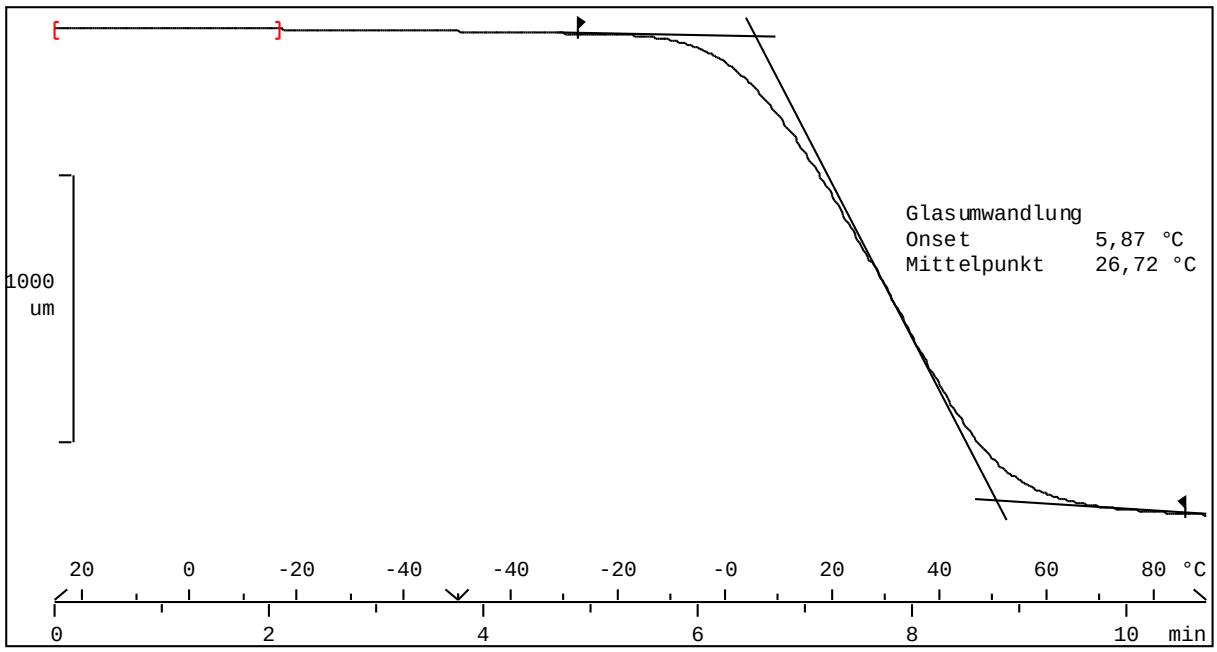
^{13}C NMR ($CDCl_3$): δ = 24 (1C, $(CH_3)_2$); 38 (1C, -C-S-); 119 (-CN); 127-142 (6C, phenyl group).

EI mass spectrum: found, 221.34 (M^+); $C_{11}H_{11}NS2$ requires 221.03.

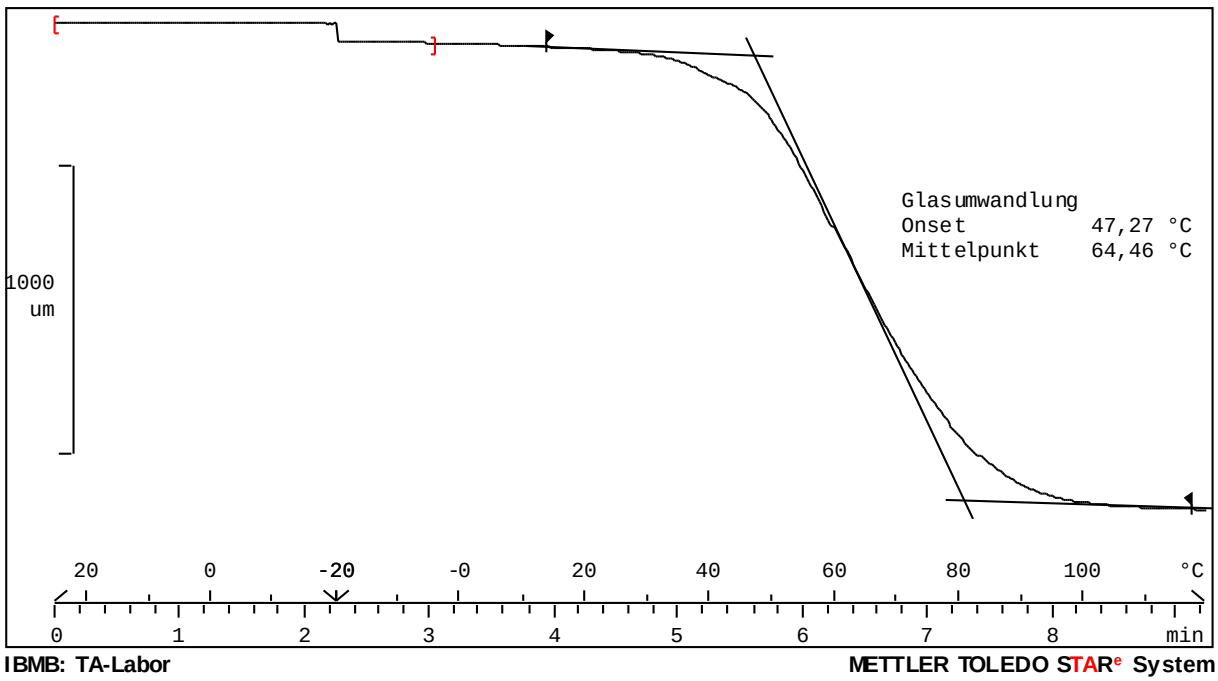
Mass Spectra of RAFT agents



Appendix 6. Thermal mechanical analyses (TMA)



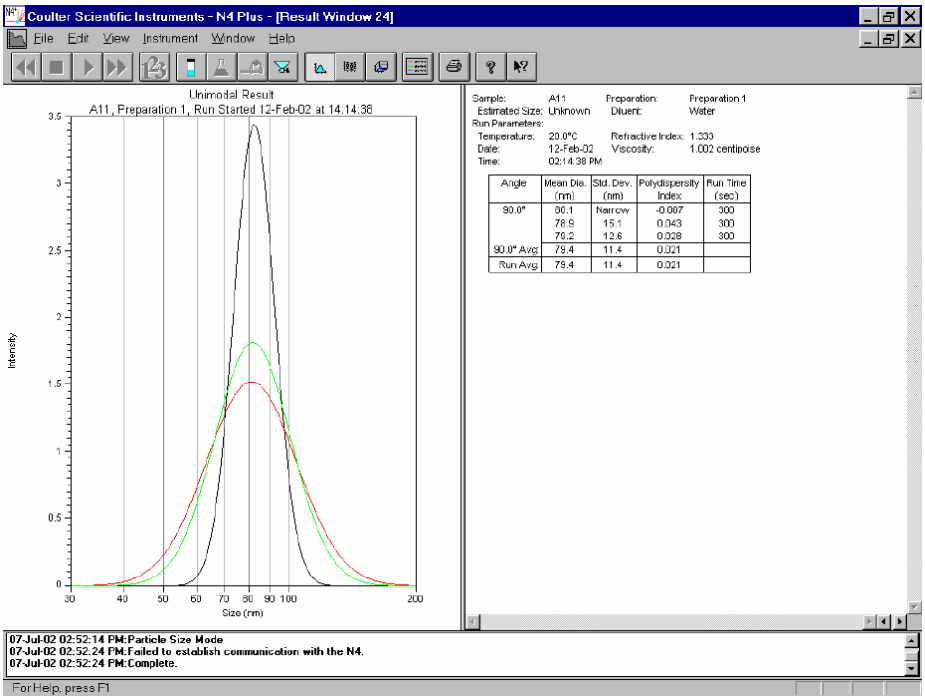
Thermal mechanical diagram of 3-MDG/BA (20/80 wt.%) copolymer prepared by semicontinuous emulsion polymerization with the pre-emulsion technique.



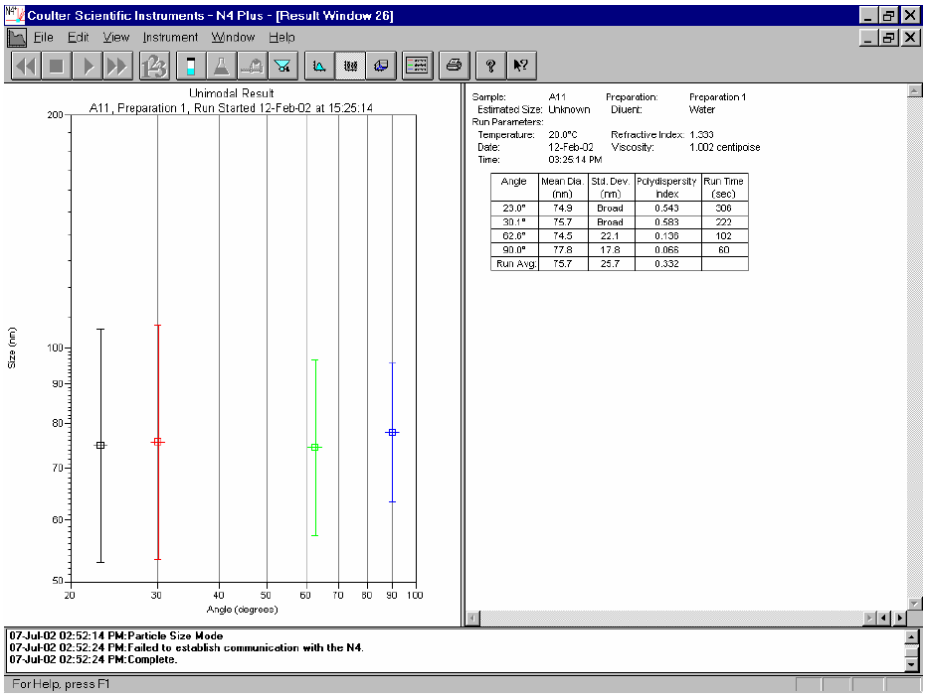
Thermal mechanical diagram of 3-MDG/BA (35/65 wt.%) copolymer prepared by semicontinuous emulsion polymerization with the pre-emulsion technique.

Appendix 7. Particle size measurement by Coulter Scientific Instruments-N4 Plus

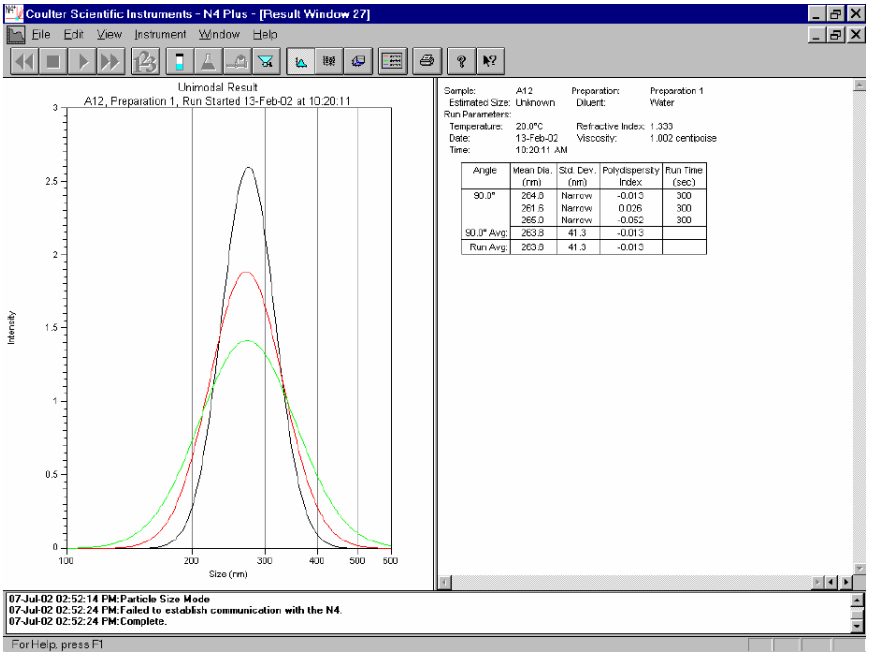
A) Particle size of monodisperse latex prepared by pre-emulsion technique with [SDS] of 10 g/l and E_c=20% (see page 84). The particle size is 79.1 nm and the particle size distribution is 0.022.



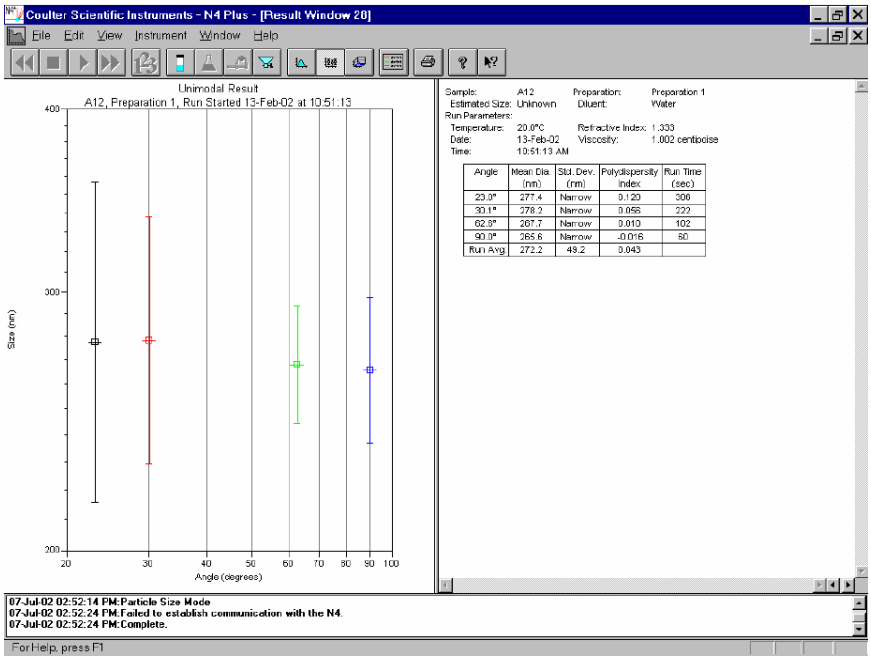
B) The same sample was measured at 4 different scattering angels (23, 30, 63 and 90°) and the deviations show below confirms the average D and the narrow particle size distribution.



C) Another particle size of monodisperse latex prepared by pre-emulsion technique with [SDS] = 1g/l, (below the CMC) (see page 84). At 90°, the average particle size is 263 nm and exhibits a very narrow particle size distribution.



D) The same sample was measured at different scattering angels (23, 30, 63 and 90°) and the deviations show below confirms the average D and the narrow particle size distribution.



Appendix 8. Calculation of conversion by semicontinuous polymerization

Conversion by GC-method

1. Instantaneous conversion (X_{INS})

a) without seed stage $$X_{INS} = \frac{R_m t - M_t}{R_m t} \quad (1)$$

where, R_m is the monomer feed rate (g/min), t is the time, M_t is the amount of monomer in the reactor in (g), which was measured by GC.

b) with seed stage $$X_{INS} = \frac{M_0 + R_m t - M_t}{M_0 + R_m t} \quad (2)$$

where, M_0 is the amount of monomer in (g), which was added at the outset of polymerization.

2. Overall or total conversion (X_T)

a) without seed stage $$X_T = \frac{R_m t - M_t}{M_T} \quad (3)$$

where, M_T is the total amount of monomer(s) in (g), that added before and during the polymerization.

b) with seed stage $$X_T = \frac{M_0 + R_m t - M_t}{M_T} \quad (4)$$

Conversion by gravimetric method

1. Instantaneous conversion; $$X_{INS} = \frac{T_{s,Exp.,t}}{T_{s,Theo.,t}} \quad (5)$$

where; $T_{s,Exp.,t} = \frac{M_{dry\ latex}}{M_{wet\ latex}}$ and

$$T_{s,Ther.,t} = \frac{(M_M + M_E + M_I + M_P)_0}{(M_M + M_W + M_E + M_I + M_P)_0} + \frac{\sum(M_M + M_E + M_I + M_P)_t}{\sum(M_M + M_W + M_E + M_I + M_P)_t} \quad (6)$$

where, M_M, M_W, M_E, M_I, and M_P are the amounts of monomer, water, emulsifier, initiator and buffer, respectively. $\frac{(M_M + M_E + M_I + M_P)_0}{(M_M + M_W + M_E + M_I + M_P)_0}$, this part represents the total dry substance in the charge.

2. Overall conversion $X_T = \frac{T_{s,Exp.,t}}{T_{s,Theo.,T}}$

$$T_{s,Ther.,T} = \frac{(M_M + M_E + M_I + M_P)_0 + \sum(M_M + M_E + M_I + M_P)_t}{(M_M + M_W + M_E + M_I + M_P)_T} \quad (7)$$

where $(M_M + M_W + M_E + M_I + M_P)_T$ is the total dry substance in the recipe.

Appendix 9. Gas chromatography (GC) conditions

The individual monomer conversion was followed by gas chromatography (GC). The apparatus consists of a GC 14-B unit, hydrogen flame ionization detector (FID), auto sampler AOC-17 and capillary column. The capillary column, with a length of 50 m, 0.32 mm inner diameter and a layer thickness of 0.5 µm, was filled with Crossbond-95%-dimethyl-5%-diphenyl polysiloxan, as a stationary phase. The measurements were carried out with two steps heating program (see Table 1). Nitrogen was used as a carrier gas with a pressure of 100 kPa. Hydrogen and air pressure were 60 kPa and 50 kPa, respectively. For the preparation of the samples, about 1 ml latex was diluted with 1 ml methanol in order to precipitate the polymer, which has been separated by centrifugation (15000 rpm) and then a definite amount of toluene, as internal standard, was added to the solution.

Table 1. GC-heating program.

Initial temperature	[°C]	50
Isothermal phase	[Min]	10
Program rate (1)	[°C/min]	16
Final temperature (1)	[°C]	120
Isothermal phase	[Min]	0
Program rate (2)	[°C/min]	20
Final temperature (2)	[°C]	230
Isothermal phase (2)	[Min]	10

To determine the method factor, standard solution was prepared from 0,01g internal standard (toluene), 0.1 g MDG and 0.1 g BA was weighed accurately and dissolved in 2ml Methanol. The standard solution was injected three times and the middle value was taken.

The amount of the monomer was calculated as follows:

$$MF_i = \frac{A_s * m_i}{A_i * m_s} \qquad \text{and} \qquad W_i = \frac{MF_i . A_i . m_s}{m_{sample} . A_s} * 100$$

where, MF_i is the method factor for the component i, A_i is the peak area of component I, w_i is the weight of component i in the sample in %, m_i is weight of component i in the standard solution, and m_{sample} is the weight of sample.

CURRICULUM VITAE

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